^{14}N Nuclear Quadrupole Coupling in Heterocyclic Compounds, Part 2. A Comparison of *ab initio* Calculations and Experimental Results for the Azoles and Azines

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Ab initio calculations of double zeta quality have been reported for the conjugated 5- and 6-membered ring heterocycles containing NH and NMe groups. The electric field gradients were calculated and the derived nuclear quadrupole coupling constants (NQCC) compared, both in magnitude and direction, with those obtained by microwave spectroscopy and by nuclear quadrupole resonance. A comparison of the results with those of the corresponding O- and S-heterocycles, and with acyclic compounds has been given, and it was shown that aromaticity considerations were of no relevance to the NQCC values at pyridine-like *N*; planarity of the *N* atom at *N*-1 in the systems 2c–9c is responsible for the very low magnitude of χ_π, and this is clearly associated with the level of π-donation from *N*-1; this is a function of position of the other ring *N* atoms, and appears to become saturated as the ring positions become predominantly *N*. In particular three contiguous *N* atoms seem to have less effect than two *N* atoms.

1. Introduction

Recently we reported [1] the quadrupole coupling results of a combined study by ^{14}N nuclear quadrupole resonance (NQR) and *ab initio* molecular orbital calculations for a variety of aza-derivatives of the 5-membered ring O- and S-heterocycles, 1–7 with X=O (O-Series) and X=S (S-Series). Closely related to these ring systems are the aza-derivatives of pyrrole (1c) (NH-Series) and its N-methyl derivative (1d) (NMe-Series), including the tetrazoles (8a, b; 9a, b) where the parent compounds of the O- and S-series are not yet known. We will also be including in this paper the results and discussion of nuclear quadrupole coupling constants (NQCC) in the azines 10–14. We mention at the outset that it had been hoped to include a study of the NQR spectra of the NH and NMe series, but that the interpretation of the spectra proved an impossible task in view of the piezo-electric character of many of the compounds [2–4].

Whereas the O- and S-Series were all single substances, the NH Series are capable of tautomerism, and the dominant tautomer varies with the phase or solvent in some instances. Thus we studied theoretically the NMe series (as well as the NH ones), since these compounds are the ones which are most likely to be amenable to experimental study by either microwave spectroscopy (MW) or NQR and which exhibit the intrinsic properties of the ring system. For 1,2,3-triazole (5c, 6c), the most abundant form in solution is the 1H-tautomer (6c) [5]; this was the form first observed in the gas phase MW spectrum [6, 7] but it is no longer thought to be the dominant isomer there [8]. This last conclusion arises from the relative dipole moments (μ) of the 1H-(6c) and 2H-(5c) forms (4.38 and 0.21 D respectively); since the MW intensity varies with μ^2, a ratio of the 2H:1H forms near to 100:1 seems probable [8]. The position with the tetrazoles (8a, 9a) seems to be equally complex, since there the MW spectra of different tautomers were thought to be dominant when differing isotopic enrichments were present [9]; this unlikely proposal is most sensibly rationalised in terms of varying properions of the tautomers in different spectral conditions. In the solid state tetrazole exists as the 1H-isomer (8a) [10]. However, other recent work on the UV-photoelectron spectra supports the dominance of the 2H form for both 1,2,3-triazole (6c) and tetrazole (9a) in the gas phase at 30 °C [11]. It appears that 1,2,4-triazole exists in the 1H-rather than the 4H-form under most conditions [11–13] (see scheme 1 on p. 43).

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2. Computational and Theoretical Methods

2(a) *Basis Sets*

All of the present calculations used the same double zeta basis of gaussian orbitals as our previous work [1]; this is a 9s/5p set completely uncontracted in the valence shell [14], and thus the results of the two investigations are completely comparable.

2(b) *Molecular Structures*

Where possible MW structures were used on the grounds that direct comparison with the MW nuclear quadrupole coupling constants (NQCC) is intended; the compounds studied by this method are: pyrrole (1c) [15], pyrazole (2c) [16], and 1,2,4-triazole (7c) [13], pyridine (10) [17] and pyridazine (11) [18]; the results of other determinations were used for imidazole (3c) [19a], tetrazole (8a) [10], pyrimidine (12) [19b], pyrazine (13) [20] and tetrazine (14) [21]. It has been noted previously that bond lengths and angles in 5-membered ring heterocycles are often transferable between molecules having the same molecular fragment [22—27]; in this light we have been able to construct reasonable geometries for the other members of the present work; N-methyl groups were incorporated using the lengths in N-methylpyrrole [28] and assuming the CH_3 lies along the NH axis.

2(c) *Theoretical Description of Electric Field Gradients* (EFG)

Most of the background for this work is given in Reference [1]; here we just note for completeness that NQR spectroscopists usually refer to their principal axis (PA) NQCC (χ_{ii}, where $i = x, y, z$) with the convention $|\chi_{zz}| > |\chi_{yy}| > |\chi_{xx}|$. The asymmetry parameter (η) is given by Eq. (1), and the Laplace relationship (Eq. (2)) also holds. In MW spectroscopy the inertial axes (IA) a, b, c, lead to χ_{ii} with $i = a, b, c$; in suitable cases this *inertial axis* data can be converted to PA data if the off-diagonal elements χ_{ab} etc. ($a \neq b \neq c$) can be obtained. The NQCC tensor is traceless in both the PA and IA systems. The computational method leads from the wave-function to the six elements of the electric field gradient (q_{ij}); this can be diagonalised to the PA values, and it is also possible to compute in any convenient alternative axis system (such as the IA system). Thus in cases where the MW spectra have only yielded IA values for χ_{ii}, we can compare with corresponding calculated IA values. In order to express the EFG in MHz, the experimental units for NQCC via Eqs. (3—5), we need the value of the ^{14}N atomic quadrupole moment (Q_N); this cannot be derived exactly [1], but our previous work [1] showed that good numerical values of the NQCC were obtained from the calculated EFG when $Q_N = 0.0167$ barn, and this value is adopted in the present work. For other basis sets it may be necessary to use different values for Q_N. It is worth noting that the EFG is a difficult property to calculate accurately, and this is confirmed by the lack of usage of quantum mechanical calculations for this purpose. A typical example of the difficulty is exemplified by pyrrole (1c); if we express the coordinate system with NH bond in a *radial* (R) direction, a *tangential* (T) direction at N in the molecular plane and a π-direction mutually perpendicular [1], we have χ_R, χ_T and χ_π to evaluate. Experimental MW values are 1.45, 1.21 and −2.66 MHz respectively; the present double zeta basis gives good agreement (Table 4), but the CNDO-2 method [29] yields 4.91, 1.96 and −6.87 MHz respectively; CNDO-2D gives [30] 3.39, 1.28 and −4.67 MHz; minimal basis *ab initio* calculations [31] give 2.34, 2.92 and −5.26 MHz.

$$\chi_{zz}|\eta| = \chi_{zz} - \chi_{yy}, \tag{1}$$

$$\chi_{xx} + \chi_{yy} + \chi_{zz} = 0, \tag{2}$$

$$\chi_{zz} - \chi_{yy} = e^2 Q_N |q_{zz} - q_{yy}|, \tag{3}$$

$$\chi_{zz} - \chi_{xx} = e^2 Q_N |q_{zz} - q_{xx}|, \tag{4}$$

$$\chi_{xx} - \chi_{yy} = e^2 Q_N |q_{xx} - q_{yy}|. \tag{5}$$

3. Results and Discussion

3(a) *Total Energy and Tautomerism*

A comparison of the total energies (1 a.u. = 627 kcal mol^{-1} = 2626 kJ mol^{-1}) (Table 1) for the present molecules with earlier calculations shows that, with the exception of single calculations on pyrazole (2c), and pyrazine (13), the present values are significantly lower than previous work. The results suggest that the 2H-form of 1,2,3-triazole (5c) should be thermodynamically more stable (by about 16 kcal mol^{-1}) than the 1H-form (6c) in the isolated state (e.g. the gas phase at low pressure); this is consistent with the recent observation of the

Table 1. Total Energies.

Molecule	Total Energy (a.u.)	Other Literature Values (a.u.)
pyrrole (1c)	– 208.74090	– 207.93070[d] – 208.26263[a] – 206.8[c] – 207.9314[b]
1-methylpyrrole (1d)	– 247.75120[h] – 247.75106[i]	
pyrazole (2c)	– 224.71063	– 224.6499[f] – 224.7401[g] – 223.823[e] – 224.3185[t] – 223.7327[a]
1-methylpyrazole (2d)	– 263.70731	
imidazole (3c)	– 224.72709	– 224.6672[f] – 223.849[e] – 224.3271[f] – 223.9347[a]
1-methylimidazole (3d)	– 263.73854	
1H-1,2,3-triazole (6c)	– 240.63704	– 239.8499[a]
1-methyl-1,2,3-triazole (6d)	– 279.66126	
1H-1,2,4-triazole (7c)	– 240.69092	– 239.8033[a]
1-methyl-1,2,4-triazole (7d)	– 279.70693	
2H-1,2,3-triazole (5c)	– 240.66446	
2-methyl-1,2,3-triazole (5d)	– 279.68979	
4H-1,2,4-triazole (4c)	– 240.67734	
4-methyl-1,2,4-triazole (4d)	– 279.68904	
1H-tetrazole (8a)	– 256.60344	– 255.8008[a]
1-methyltetrazole (8b)	– 295.62796	
2H-tetrazole (9a)	– 256.61827	
2-methyltetrazole (9b)	– 295.64678	
Pyridine (10)	– 246.6053	– 245.7649[j] – 245.622[k] – 246.327[i] – 246.417[m] – 246.5491[o]
Pyridazine (11)	– 262.5429	– 261.685[j] – 262.313[m] – 262.4744[o]
Pyrimidine (12)	– 262.5785	– 261.6787[j] – 262.361[m] – 262.5132[o]
Pyrazine (13)	– 262.5513	– 261.554[k] – 262.255[l] – 262.352[m] – 262.5731[n] – 262.5107[o]
1,2,4,5-Tetrazine (14)	– 294.4516	– 293.4748[j] – 294.150[m] – 294.3661[o]
trans-NH$_2$OH (22)	– 130.9494	– 130.9882[p] – 130.8974[q] – 129.7061[r]
cis-NH$_2$OH	– 130.9316	– 130.8802[q] – 129.6944[r]
trans-NH$_2$SH (23)	– 453.6582	– 452.9481[s]
gauche-N$_2$H$_4$ (24)	– 111.1333	– 111.1239[r] – 111.1815[p] – 111.0743[q]
gauche-MeNHNH$_2$ (25)	– 150.1358	–
Vinylamine (21)	– 133.0178	– 132.5415[t]

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2H-isomer in the MW spectrum (cf above ([8]. In contrast, the unsymmetrical 1H-form (7c) of the 1,2,4-isomer is energetically preferred (Table 1) by about 8 kcal mol^{-1} over the symmetrical 4H-form (4c); this is again in agreement with both MW and solution data [12, 13]. The energetic preference

(Table 1) for the 2H-form of tetrazole (9a) relative to the 1H-form (8a) contrasts with the known crystal structure [10] and with the usual interpretation of the ^1H NMR spectrum [32]; again however, there appears to be agreement with the gas phase, where the UV-photoelectron spectrum of the tautomeric mixture is very similar to that of 2-methyltetrazole (9b) and distinctly different to the 1-methyl compound (8b) [11]. The present calculations, and some previous ones (Table 1) suggest that pyrimidine (12) is thermodynamically more stable than its isomers (11 and 13).

3(b) *Electric Field Gradients*

In Table 2 we give the computed results of the EFG calculations in atomic units (1 a.u. $= 0.324123 \times 10^{16}$ esu · cm^{-3}). These will normally be directly comparable with other calculated data [33], but in the present instance the only other *ab initio* results, using a large enough basis set to yield reasonable values [34], gives results in the PA using the convention $|q_{zz}| > |q_{yy}| > |q_{xx}|$, but with inadequate information concerning the relationship of (x, y, z) with molecular or inertial axes; only in some cases (using correlation with experiment, and symmetry) can this information be deduced. It is important for comparison of results in this area that the non-zero elements of the rotation matrix between the cartezian and the PA directions are given.

3(b) (i). *Directions*

As previously [1] we define the out-of-plane axis as π, and the two in-plane axes as R and T where these refer to Radial and Tangential axes at the N atom in question (i.e. local axes). In molecules where the N atom lies on a C_2 symmetry axis, the corresponding χ_{ii} (χ_R and χ_T) lie exactly along R and T (e.g. 1c, d, 4c, d, 5c, d). In less symmetrical molecules we refer to χ_R as that EFG/NQCC whose principal axis is closest to R. The angle between R and χ_R is then $\theta°$ and has sign as well as magnitude; we adopt our previous convention that θ is positive when the angle θ makes the EFG rotate from R towards the adjacent centre responsible for the distortion in position.

The present results are shown in Fig. 1 and Table 3; similar results for the O- and S-series are given in Fig. 1 of Reference [1]. In all cases where MW data is available, the agreement with the calculated values is good. In the present NH-series the average difference (11 centres in total) between the calculated and observed directions ($\theta_{calc} - \theta_{obs}$) is 4°, and the maximum difference is 9° (7c, see below); a similar accuracy was obtained with our previous calculations (10 centres) on the O- and S-series [1]. Thus in the cases where no experimental data is available, the calculations *at least* can be expected to produce meaningful trends and gross changes. An example where these calculated data may indicate further experimental work is 1H-1,2,4-triazole (7c); a full MW substitution structure has not been obtained for this molecule, although an estimated one which was consistent with the moments of inertia has been given [13]; the position of χ_R is satisfactory at $N-1$, but there are substantial differences at $N-2/N-4$ [35] which suggests that the estimated angles at these centres may require further optimisation. The situation with N-methylpyrrole (1d) is also unsatisfactory and this is discussed below.

The systematic trends observed in our previous work [1] on the O- and S-heterocycles also apply to the NH and NMe compounds for pyridine-like nitrogen ($\geqq N$:). Thus if we take the series 2a—2d containing the fragment (—X—N=) (α-nitrogen), we find that χ_R is rotated towards X by about 25° (X=O) or 15° (X=S, NH, NMe). When the N atom is in a β-position (—X—CH=N—) with respect to X, then χ_R lies within a few degrees of the external bisector R; again there is a larger value of θ for X=O (3a) than X=S, NH or NMe (3b, c, d). If very small calculated differences are significant, then we have for $|\theta|$ in each N-type X=O > X > NH > NMe.

3(b) (ii) *Magnitudes*

A direct comparison of the calculated and observed NQCC was used in our previous work to establish a value for Q_N such that numerical agreement between the χ_{calc} and χ_{obs} was optimal. The fit of data was good (see Fig. 2 of Ref. [1]). This data (25 points) can now be extended to include data for 1d, 2c, 3c, 6c and 7c (60 points) and is shown in Figure 2. It is clear that the value of Q_N is unchanged, and the new points are in positions such that the linearity of the data is further strengthened. A single major discrepancy is apparent viz. 1-methylpyrrole (1d); the MW spectrum has yielded two different sets of NQCC [28, 15

Table 2. Calculated ^{14}N Electric Field Gradients (a.u.).

Compound		E_R	E_T	E_π	Asymmetry Parameter
Pyrrole		−0.4009	−0.3753	0.7763	0.0326
1-Methylpyrrole		−0.4523	−0.3509	0.8035	0.1258
Pyrazole	N1	−0.2877	−0.5930	−0.8805	0.3465
	N2	1.1173	−0.9102	−0.2074	0.6291
1-Methylpyrazole	N1	−0.3391	−0.5654	0.9045	0.2500
	N2	1.0850	−0.9034	−0.1813	0.6654
Imidazole	N1	−0.3836	−0.3660	0.7493	0.0235
	N3	1.0564	−0.5468	−0.5096	0.0351
1-Methylimidazole	N1	−0.4231	−0.3470	0.7701	0.0988
	N3	1.0598	−0.5462	−0.5136	0.0304
1H-1,2,3-Triazole	N1	−0.2304	−0.4809	0.7113	0.3518
	N2	1.1619	−1.0027	−0.1592	0.7259
	N3	1.3395	−0.7423	−0.5972	0.1083
1-Methyl-1,2,3-triazole	N1	−0.1929	−0.4804	0.6730	0.4285
	N2	1.1289	−0.9780	−0.1512	0.7322
	N3	1.3389	−0.7556	−0.5833	0.1285
1H-1,2,4-triazole	N1	−0.2928	−0.6557	0.9485	0.3826
	N2	1.1385	−0.9981	−0.1405	0.7926
	N3	1.1015	−0.5652	−0.5363	0.0262
1-Methyl-1,2,4-triazole	N1	−0.2991	−0.6529	0.9522	0.3717
	N2	1.1012	−0.9689	−0.1319	0.7601
	N3	1.1010	−0.5632	−0.5374	0.8201
2H-1,2,3-Triazole	N1	1.2229	−0.8228	−0.4001	0.3452
	N2	−0.3445	−0.7360	1.0804	0.3628
	N3	1.2229	−0.8228	−0.4001	0.3452
2-Methyl-1,2,3-triazole	N1	1.1931	−0.8103	−0.3824	0.3589
	N2	−0.2948	−0.7499	1.0450	0.4355
	N3	1.1931	−0.8103	−0.3824	0.3589
4H-1,2,4-Triazole	N1	1.0285	−0.7862	−0.2426	0.5286
	N2	1.0285	−0.7862	−0.2426	0.5286
	N3	−0.3992	−0.4818	0.8809	0.0936

Table 2 (continued).

Compound		E_R	E_T	E_π	Asymmetry Parameter
4-Methyl-1,2,4-triazole	N1	1.0325	−0.7902	−0.3824	0.5303
	N2	1.0325	−0.7902	−0.3824	0.5303
	N3	−0.4304	−0.4690	0.8992	0.0429
2H-Tetrazole	N1	1.2237	−0.9201	−0.3036	0.5037
	N2	−0.2746	−0.6126	0.8872	0.3817
	N3	1.3205	−0.8342	−0.4860	0.2635
	N4	1.2575	−0.7976	−0.4599	0.2684
2-Methyltetrazole	N1	1.1854	−0.9065	−0.2789	0.5294
	N2	−0.2034	−0.6176	0.8208	0.5043
	N3	1.2799	−0.8248	−0.4551	0.2885
	N4	1.2504	−0.8075	−0.4429	0.2915
1H-Tetrazole	N1	−0.1895	−0.5272	0.7167	0.4714
	N2	1.2649	−0.9565	−0.3081	0.5124
	N3	1.1619	−0.7868	−0.3748	0.3546
	N4	1.2606	−0.8197	−0.4412	0.3000
1-Methyltetrazole	N1	−0.1387	−0.5288	0.6776	0.5842
	N2	1.2246	−0.9366	−0.2882	0.5296
	N3	1.1647	−0.8044	−0.4525	0.2857
Pyridine	N1	1.2645	−0.4573	−0.8072	0.2770
Pyridazine	N1/2	1.4382	−0.6359	−0.8023	0.1160
Pyrimidine	N1/3	1.1762	−0.4850	−0.6912	0.1750
Pyrazine	N1/4	1.3035	−0.3809	−0.9227	0.4160
Tetrazine	N1/2/3/4	1.4947	−0.5823	−0.9124	0.2210
Hydroxylamine	N1	−1.2995	−0.1346	1.4341	0.8120
Thiohydroxylamine	N1	−0.4147	−0.7117	1.1264	0.2640
Hydrazine	N1	−1.0618	−0.4162	1.4779	0.4367
Methylhydrazine	NHMe	−1.1037	−0.4776	1.5813	0.3960
	NH_2	−1.0767	−0.4430	1.5198	0.4170
Vinylamine	N1	1.2903	−0.5822	−0.7081	0.0975

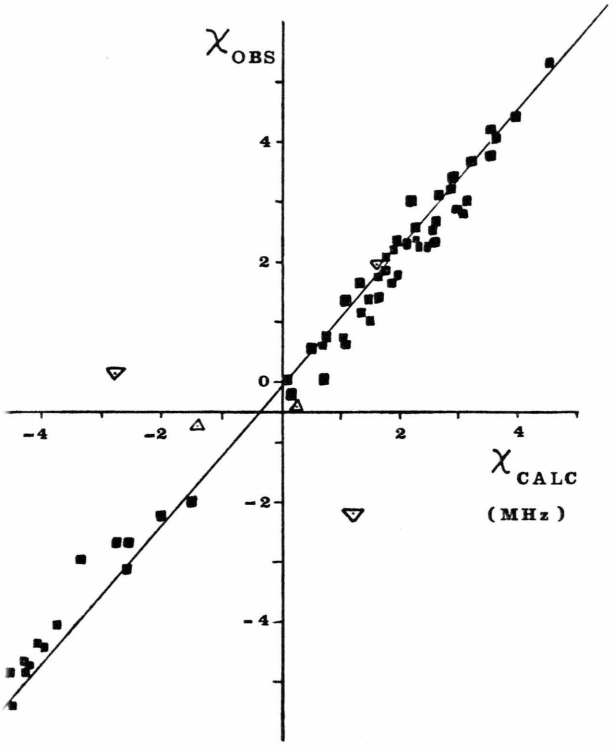


Fig. 1. Correlation of calculated and experimental nuclear quadrupole coupling constants. Both IA and PA data are included. Points marked ▽ refer to 1-methyl-pyrrole (1d), while those for 1,2,5-oxadiazole (5a) are marked △; both these latter series are thought to have incorrect experimental values.

(footnote on revised data)]. One coupling is largely unchanged in these two analyses, but the other differences are more significant and involve a change of sign for χ_π; neither set yields results even close to the present calculated values and a re-investigation of the MW spectrum seems appropriate; it is worth noting that the NQR experiment yields [4] values for the three couplings which are consistent both with those for pyrrole (1c) and the calculations (Table 3). A further feature of the MW data is the value for η (either 0.64 or 0.82); this seems to be singularly high for N attached to three C atoms, even allowing for the fact that two are part of a conjugated system; we take this point up below, but typical values for η in simple amines with differing numbers of C atoms attached are: $-NH_3$ (0.0), $MeNH_2$ (0.186), Me_2NH (0.169) and Me_3N (0.0).

Much of the discussion on variations in magnitude of $|\chi_{ii}|$ in our previous paper [1] is valid here, and thus we note only a few generalisations. In Section IV we attempt to obtain values for χ_{ii} in simple aliphatic molecules, and to then determine whether the values of the cyclic systems (1—9) indicate any non-local effects. The magnitude of $|\chi_R|$ for molecules containing the group $(-X-N=)$ varies according to the nature of X, such that $O > S = NH > NMe$ in the 1,2—(2), 1,2,5—(5) and 1,2,3—(6) compounds. In the grouping

Table 3. Comparison of ^{14}N Nuclear Quadrupole Coupling Constants (MHz) by Various Methods.

Compounds	N site	Method	Coupling Constants (MHz)			Asymmetry	Rotation	Ref.ᵃ
			χ_R	χ_T	χ_π	η	Θ	
Pyrrole 1(c)	N1	a) Calc.	1.413	1.323	−2.736	0.0326	0.0	—
		b) NQR	1.308	0.754	(−)2.062	0.2688	0.0	[3]
		c) MW	1.45	1.21	−2.66	0.0902	0.0	[15]
		d) Calc.	2.341	2.916	−5.257	0.109	0.0	[31]
1-Methyl-pyrrole 1(d)		a) Calc.	1.594	1.237	−2.832	0.1258	0.0	—
		b) MW	1.97	−2.16	0.19	0.824	0.0	[28]
		c) MW	2.05	−1.69	−0.37	0.644	0.0	[15, 28]
Pyrazole 2(c)	N1	a) Calc.	1.014	2.090	−3.103	0.3465	26.0	—
		b) MW	0.72	2.30	−3.02	0.5230	28.4	[16, 64]
		c) Calc.	1.028	2.572	−3.600	0.4172	—	[34a, b]
		d) Calc.	1.883	3.045	−4.928	0.236	—	[31]
	N2	a) Calc.	−3.938	3.208	0.731	0.6291	15.5	—
		b) MW	−4.48	3.69	0.79	0.6473	17.5	[16, 64]
		c) Calc.	(−)3.9948	3.3096	0.6852	0.6572	—	[2, 3]
		d) Calc.	−4.405	3.445	0.960	0.564	—	[34b]
		d) Calc.	−4.928	3.045	1.883	0.236	—	[31]

Table 3 (continued).

Compounds	*N* site	Method	Coupling constants (MHZ) χ_R	χ_T	χ_π	Asym-metry η	Rotation Θ	Ref.[a]
1-Methyl-pyrazole 2(c)	N1	a) Calc.	1.195	1.993	−3.188	0.2500	32.1	—
	N2	a) Calc.	−3.824	3.184	0.639	0.6654	16.7	—
Imidazole 3(c)	N1	a) Calc.	1.352	1.290	−2.641	0.0235	9.8	—
		b) NW	1.494	1.043	−2.537	0.1778	17.0	[53]
		c) NQR	1.4098	0.0142	−1.424	0.980		[65]
		d) Calc.	1.361	1.659	−3.020	0.099	—	[34a, b]
		e) Calc.	2.395	1.920	−4.315	0.110	?	[31]
	N3	a) Calc.	−3.723	1.927	1.796	0.0352	0.0	—
		b) MW	−4.032	1.774	2.258	0.1200	4.0	[53]
		c) NQR	−3.267	1.844	1.423	0.129		[65]
		d) Calc.	−4.252	1.994	2.258	0.062	?	[34a, b]
		e) Calc.	−5.046	1.451	3.596	0.425	?	[31]
1-Methyl-imidazole 3(d)	N1	a) Calc.	1.491	1.223	−2.714	0.0988	0.50	—
	N3	a) Calc.	−3.735	1.925	1.810	0.0304	0.30	—
1H-1,2,3-Triazole 6(c)	N1	a) Calc.	0.812	1.695	−2.507	0.3518	44.1	—
		b) MW	0.27	3.58	−3.86	0.858	~ 50	[7]
	N2	a) Calc.	−4.095	3.534	0.561	0.7259	7.0	—
		b) MW	−4.33	3.79	0.53	0.752	~ 23	[7]
	N3	a) Calc.	−4.721	2.616	2.105	0.1083	11.9	—
		b) MW	−4.87	2.68	2.19	0.101	22	[7]
1-Methyl-1,2,3-triazole 6(d)	N1	a) Calc.	0.677	1.693	−2.372	0.4285	42.4	—
	N2	a) Calc.	−3.979	3.447	0.533	0.7322	7.1	—
	N3	a) Calc.	−4.719	2.663	2.056	0.1285	11.5	—
2-Methyl-1,2,3-triazole 5(d)	N2	a) Calc.	1.039	2.643	−3.683	0.4355	0.0	—
	N1/3	a) Calc.	−4.205	2.856	1.348	0.3589	13.7	—
2H-1,2,3-triazole 5(c)	N2	a) Calc.	1.214	2.594	−3.808	0.3628	0.0	—
	N1/3	a) Calc.	−4.310	2.900	1.410	0.3457	16.0	—
1H-1,2,4-triazole (7)	N2	a) Calc.	1.032	2.311	−3.343	0.3826	24.0	—
		b) MW	0.66	2.29	−2.95	0.553	29.1	[35]
	N2	a) Calc.	−4.012	3.518	0.496	0.7926	11.3	—
		b) MW	−4.41	3.81	0.60	0.728	~ 20	[35]
	N4	a) Calc.	−3.882	1.992	1.890	0.262	1.0	—
		b) MW	−4.01	1.80	2.21	0.102	~ 7	[35]
1-Methyl-1,2,4-triazole 7(d)	N1	a) Calc.	1.054	2.301	−3.356	0.3717	27.2	—
	N2	a) Calc.	−3.881	3.415	0.465	0.7601	17.1	—
	N4	a) Calc.	−3.879	1.985	1.894	0.0236	0.2	—
4-Methyl-1,2,4-triazole 4(d)	N4	a) Calc.	1.517	1.653	−3.169	0.0429	0.0	—
	N1/2	a) Calc.	−3.639	2.785	0.855	0.5303	13.7	—
4H-1,2,4-triazole 4(c)	N4	a) Calc.	1.407	1.698	−3.105	0.0936	0.0	—
	N1/2	a) Calc.	−3.625	2.771	−0.855	0.5286	12.6	—
1H-1,2,3,4-tetrazole 8(a)	N1	a) Calc.	0.668	1.858	−2.526	0.4714	39.9	—
	N2	a) Calc.	−4.458	3.371	1.086	0.5124	8.6	—
	N3	a) Calc.	−4.095	2.773	1.321	0.3546	1.8	—
	N4	a) Calc.	−4.443	2.889	1.555	0.3000	7.4	—
2H-1,2,3,4-tetrazole 9(a)	N1	a) Calc.	−4.313	3.243	1.070	0.5037	9.8	—
	N2	a) Calc.	2.159	0.9678	−3.127	0.3814	5.2	—
	N3	a) Calc.	−4.654	2.940	1.713	0.2635	7.2	—
	N4	a) Calc.	−4.432	2.811	1.621	0.2684	11.8	—

Table 3 (continued)

Compound	*N* site	Method	Coupling Constants (MHz)			Asymmetry	Rotation	Ref.[a]
			χ_R	χ_T	χ_π	η	Θ	
1-Methyl-1,2,3,4-tetrazole 8(b)	N1	a) Calc.	0.489	1.864	−2.353	0.5842	34.5	—
	N2	a) Calc.	−4.316	3.301	1.016	0.5296	8.7	—
	N3	a) Calc.	−4.105	2.808	1.297	0.3680	1.5	—
	N4	a) Calc.	−4.467	1.595	2.872	0.2857	7.7	—
2-Methyl-1,2,3,4-tetrazole 9(b)	N1	a) Calc.	−4.178	3.195	0.983	0.5294	5.2	—
	N2	a) Calc.	0.717	2.177	−2.893	0.5043	7.2	—
	N3	a) Calc.	−4.511	2.907	1.604	0.2889	11.8	—
	N4	a) Calc.	−4.407	2.846	1.561	0.2915	9.8	—
Pyridine (10)	N1	a) Calc.	−4.456	1.611	2.845	0.2767	0.0	—
		b) MW	−4.88	1.43	3.45	0.414	0.0	[17]
		c) NQR	−4.584	1.384	3.199	0.396	0.0	[66]
		d) Calc.	−4.11	1.29	2.82	0.375	0.0	[67]
Pyridazine (11)	N1/2	a) Calc.	−5.069	2.241	2.827	0.1157	23.3 (a, χ_R)	—
		b) MW	−5.65	2.38	3.268	0.157	20.7 (a, χ_R)	[18a]
		c) NQR	−5.188	2.814	2.374	0.085	—	[66]
		d) Calc.	−4.63	1.84	2.79	0.205	—	[67]
Pyrimidine (12)	N1/3	a) Calc. (PA)	−4.145	1.709	2.435	0.1753	0.7	—
		b) Calc. (IA)	−2.567	0.131	2.436	0.8976	—	—
		c) MW (IA)	−3.107	−0.223	3.330	0.8739	—	[68]
		d) NQR (PA)	−4.436	1.362	3.074	0.386	—	[66]
		e) Calc. (PA)	−3.87	1.32	2.55	0.315	—	[67]
Pyrazine (13)	N1/4	a) Calc.	−4.594	1.342	3.252	0.4156	0.0	—
		b) NQR	−4.857	1.127	3.73	0.536	0.0	[69]
		d) Calc.	−4.42	1.05	3.36	0.521	0.0	[67]
1,2,4,5-Tetrazine (14)	N1/2/3/4	a) Calc.	−5.268	2.051	3.215	0.2208	0.0	—
		b) Calc.	−4.79	1.61	3.17	0.324	0.0	[67]
NH_2OH (27) (cis)	N	Calc.	−5.138	4.507	0.631	0.754	19.4	—
NH_2OH (23) (trans)	N	a) Calc.	−5.054	4.580	0.474	0.812	20.0	—
		b) MW	−5.76	5.78	−0.02	0.993	—	[51]
		c) Calc.	−2.038	1.523	0.515	0.495	—	[48]
NH_2SH (24) (cis)	N	Calc. (PA)	−3.970	2.509	1.461	0.264	12.2	—
NH_2-NH_2 (25) (90°, gauche)	N	a) Calc. (IA)[b]	3.536 (aa)	−1.526 (bb)	−2.010 (cc)	0.1370	—	—
		b) MW (IA)	4.234 (aa)	−1.978 (bb)	−2.255 (cc)	0.065	—	[63]
		c) Calc. (PA)	−5.209	3.742	1.467	0.4367	12.0	—
		d) NQR (PA)	(−) 4.820	4.355	0.465	0.807	33	[36]
		e) Calc. (PA)	−2.390	1.865	0.525	0.561	—	[48]
MeNHNH$_2$ (26) gauche 26(b)	NH$_2$	a) Calc. (PA)	−5.356	3.795	1.561	0.5561	—	—
		b) Calc. (IA)[c]	−0.18	−0.57	0.75	0.9680	—	
	NMe	a) Calc. (IA)	−4.250	3.571	0.679	0.8607	—	—
		b) Calc. (PA)	−5.576	3.891	1.685	0.3960	—	
		c) MW (IA)	−4.78	4.09	0.69	0.711	—	[64]
Vinylamine (21)	N	a) Calc. (PA)	−4.547	2.052	2.497	0.0975	—	—
		b) Calc. (IA)	2.210	2.112	−4.321	0.0227	—	—
		c) MW (IA)	2.20	1.95	−4.13	0.0605	—	[47]

[a] Present work unless stated otherwise.

[b] Off-diagonal elements, not yet determined experimentally, are $\chi_{ab} + 1.038$, $\chi_{ac} - 0.708$ and $\chi_{bc} + 3.260$ MHz.

[c] Off-diagonal elements, not yet determined experimentally are $\chi_{ab} + 4.16$, χ_{ac} 1.48 and χ_{bc} 1.68 MHz. The angles between the PA and IA systems for χ_{zz} are $\Theta_{a,z}$ 46.6°, $\Theta_{c,z}$ 28.1°.

(—X—CH=N—) we find the order variation of $|\chi_R|$ with X is S > O > NH=NMe (3a—3d, 4a, b, d, 6b—6d). In general $|\chi_R|$ is larger in N—N or N=N grouping than in N—CH or N=CH, e.g. 6b, c, 3b, c; furthermore the $|\chi_R|$ coupling in (X—N_A=N_B) is larger for N_A than N_B, e.g. 6b, c, d > 4b, c, d.

4. ^{14}N NQCC in Related Aliphatic Systems

4(a) *Average Values in the Principal Axes*

In order to interpret variations in NQCC in the cyclic systems (2—9) in more detail, we need to establish norms for the coupling in small strain-free aliphatic molecules. We can then assess the effect of ring size and cyclic conjugation, and determine whether non-local contributions to χ_{ii} occur.

Unfortunately there are comparatively few principal axis (PA) results in the MW literature for χ_{ii} ($i = x, y \cdot z$), and most analyses given refer to the inertial axis (IA) with $i = a, b, c$. While the NQR data is in the PA, the directions are usually unknown, and the effects of the solid state difficult to assess; this last point is particularly important with compounds containing both $\geq$N: and >NH, because H-bonding is then a major factor. In order that we can use NQR data within the framework of isolated molecule calculations, we need to allow for temperature and condensed state effects. From comparative studies of various molecules [36], there is normally a reduction by ~15% for $|\chi_{ii}|$ on going from the MW (gas phase, room temperature) to NQR (solid, 77 °K) in non H-bonded molecules; since temperature effects operate in the reverse direction [37, 38] much of this difference can be ascribed to condensed state effects.

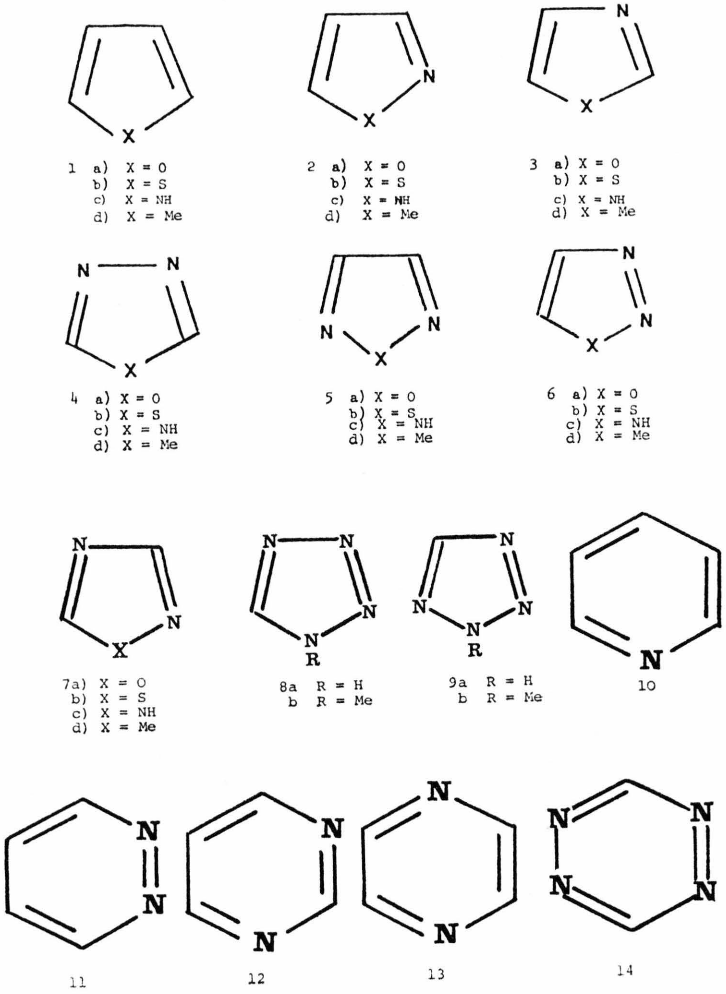
4(a) (i) Planar Nitrogen in the Imine Unit —CH=N—R

There is no MW-PA data for simple imines, but IA data has been given for the molecules 15 [39, 40], 16 [41] and 17 [42], and these are especially relevant to the present series of molecules. We have used the published geometric data [39—42] to reconstruct the IA systems shown (15—17). Owing to the planar N-atom environment, χ_{cc} is already in the PA and can be re-named χ_π; it declines from the unsubstituted value of +3.4 MHz in 17 with progressive Me substitution — a hyperconjugative effect. For both 15 and 16 the inertial b-axis lies close (especially in 16) to the external bisector of the C—N—C angle; since there are no nearby lone-pairs to distort the direction, we can take χ_{LP} to lie close to this bisector, and hence identify χ_{LP} with χ_{bb}. The value for 16 is taken owing to the better coincidence of these two axes. Thus we have χ_{LP} −5.1 MHz, χ_T (χ_{aa}, by difference) +1.9 MHz and χ_π (χ_{cc}) +3.2 MHz as normal values for the imine group.

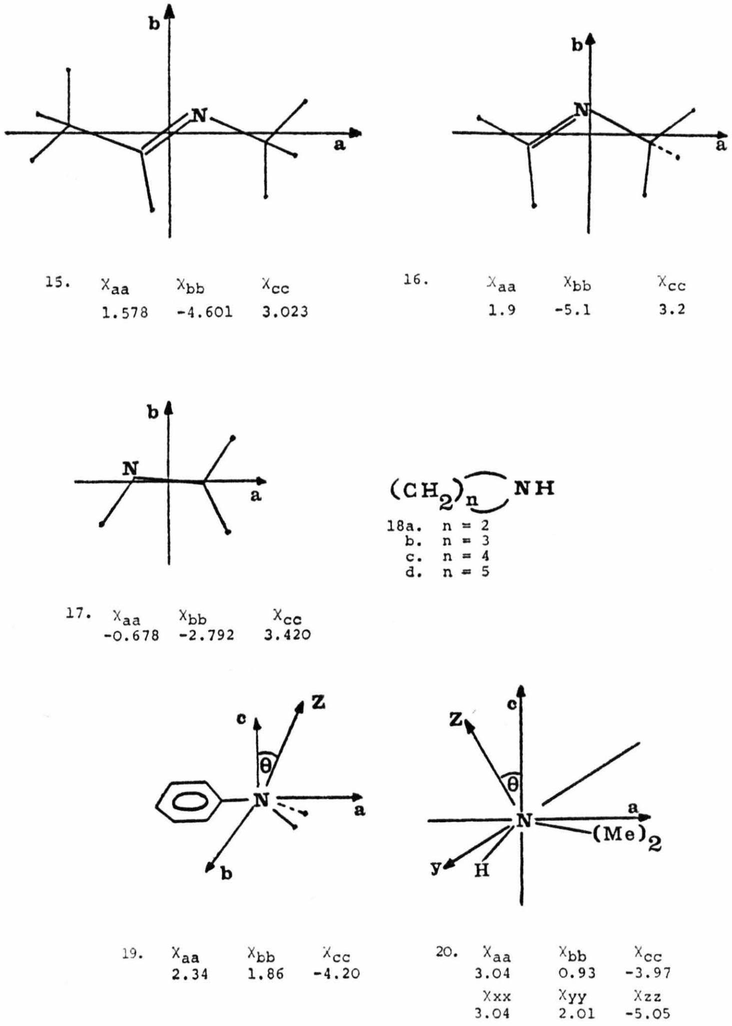
4(a) (ii) Effect of Ring, Angle Changes and Conjugation

The NQR results for a series of cyclic secondary amines (18a—d) [43] show that the values of χ_{zz} change very slowly with ring size ($n+1$), viz. −4.43 ($n=5$), −4.36 ($n=4$), −4.25 ($n=3$) and −3.58 MHz ($n=2$). All these values must refer to axes close to the lone pair, and show that ring size effects can be ignored in the 5-membered rings of the present type. If the values of χ_{zz} and η for these cyclic amines (18) are converted to yield χ_{xx} and χ_{yy} we obtain values very close to +1.5 and +2.8 MHz in each case. It is reasonable to assume that one value, say 1.5 MHz, refers to a consistent direction in each member of the series. A comparison with dimethylamine Me_2NH (19) which has χ_{zz} −4.650 MHz (solid state — a direct comparison with the above) or −5.05 MHz (MW) [44], shows that χ_{yy} bisects the C—N—C angle and lies comparatively close to the NH axis, while χ_{xx} lies parallel to the CC axis; thus we can see that the values +1.5 MHz and +2.8 MHz in the cyclic amines (18) above must be along the equivalent axes to χ_{yy} (2.01 MHz) and χ_{xx} (+3.04 MHz) of 19 respectively. These values are compared with pyrrole (1c) below.

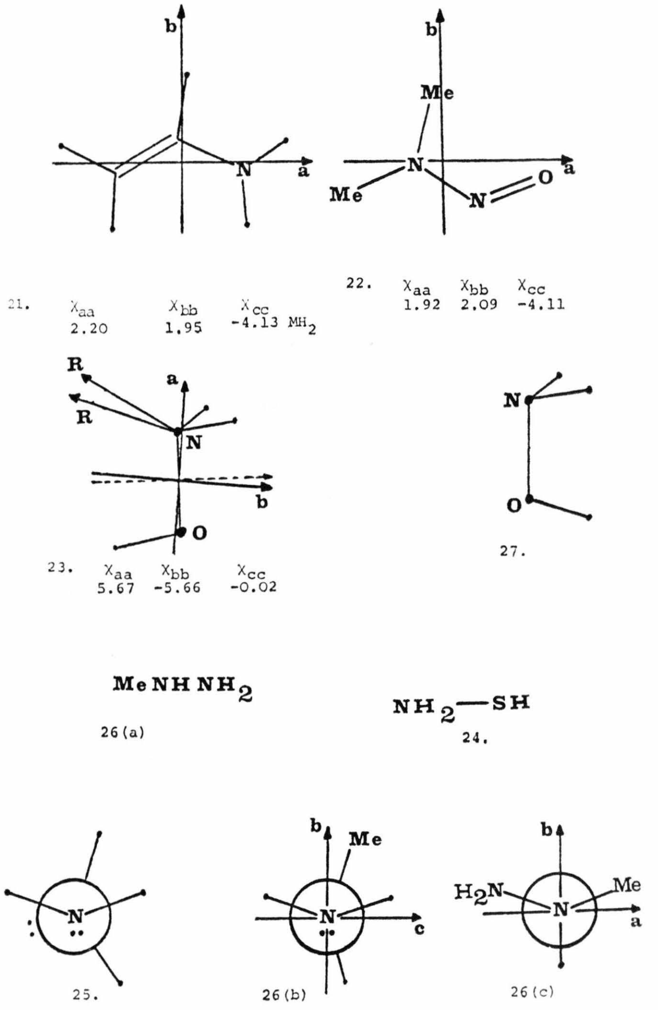
The effects of conjugation on the NQCC are more difficult to assess, since there is only data for aniline (20) [45, 46] and vinylamine (21) [47]; the MW results in the IA system yield the remarkably similar NQCC shown in 20 and 21. In the former, χ_{bb} is already a principal axis value owing to symmetry; the angle between the CN bond extension and the HNH bisector is 39° (20) and 34° (21), much lower than that in NH_3 or $MeNH_2$ [47]. This suggests that the angle (θ) between χ_π and the c-axis (20) is probably near 10°. Studies of NH_3 with fixed NH length and variable pyramid angle show [48] that as the pyramid angle *decreases* (i.e.



Scheme 1



Scheme 2



Scheme 3

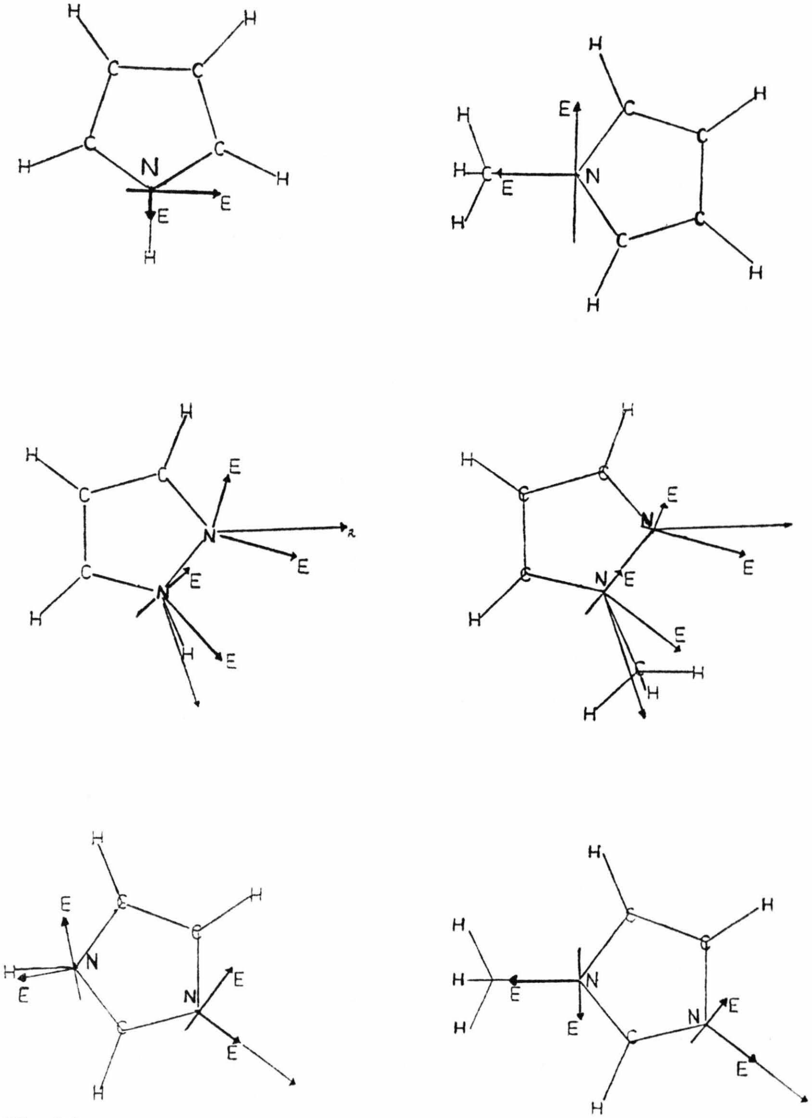


Fig. 2.1

Fig. 2. Principal in-plane axes for calculated electric field gradients (E). The radial direction (R) is shown unmarked at each centre. In some instances R and E_R coincide.

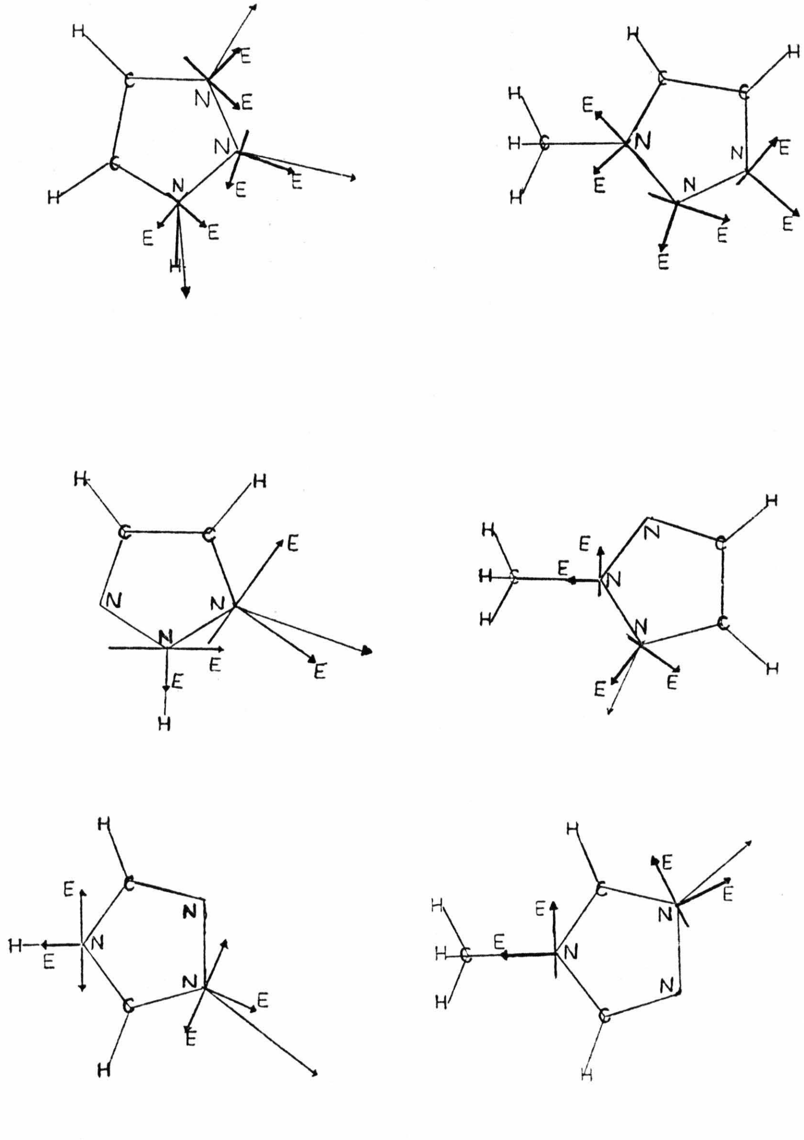


Fig. 2.2

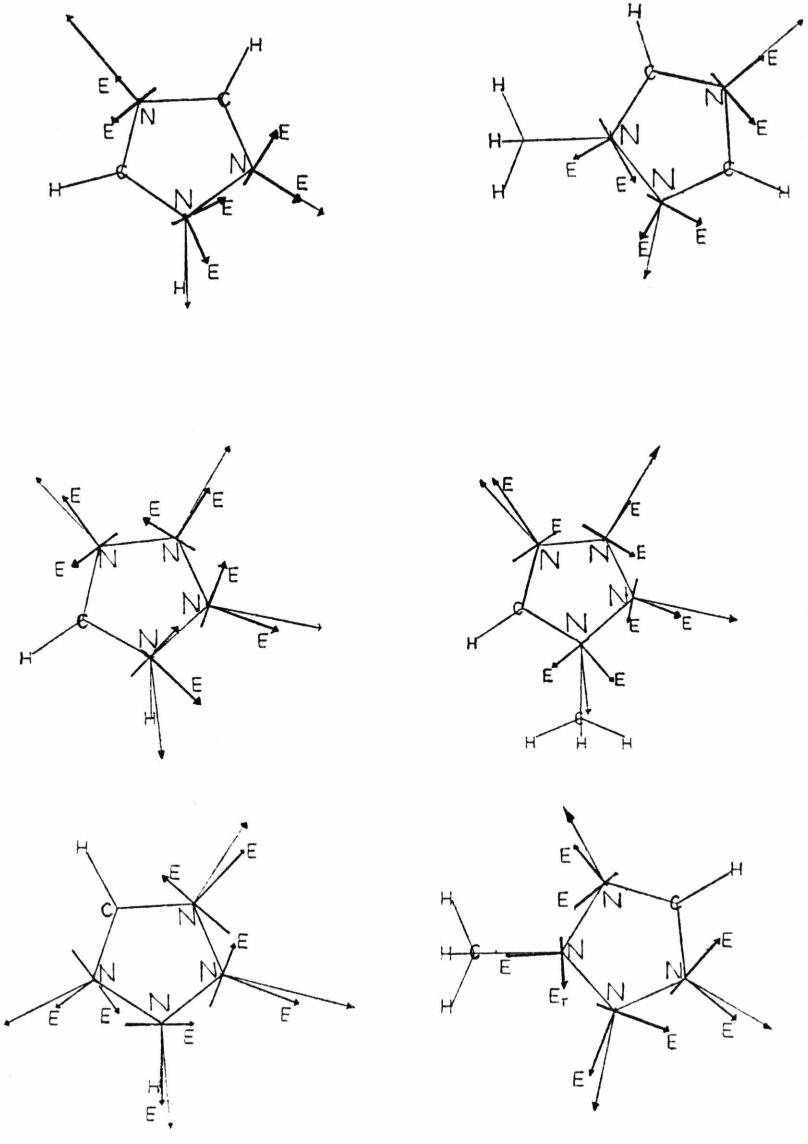


Fig. 2.3

HNH increases) so the principal EFG (and hence NQCC) *increases*. An 8° difference in HNH angle leads to an increase of χ_{zz} by 1.4 MHz [48]. The comparison of aniline (20) (or 21) with dimethylamine (19) then suggests that conjugation and the closer to planar structure in 20, working in opposite directions, have probably reduced the value of χ_{cc} (χ_π) by about 0.5 ~ 1.0 MHz, and that the conjugation effect must thus amount to a χ_π decrease of about 2 MHz. Although not an ideal system for comparison, dimethylnitrosamine (22) has planar N atoms and the IA values of the NQCC at Me_2N are as shown (22) [49, 50]. The only PA value is χ_{cc} (χ_π), and numerically this is much smaller than in aliphatic amines such as Me_2NH (19); since part of this value must arise from the substituent NO group, we conclude that a reasonable value for planar conjugated N-atoms is χ_{cc} -2.8 ± 0.2 MHz; given the traceless nature of the NQCC and the values for 19, we arrive at values of about +1.8 (χ_{xx}) and +1.0 MHz (χ_{yy}) for the two plane axes (χ_T and χ_R respectively).

4(a) (iii) Effect of the Neighbour Heteroatom

Isoxazole (2a) and 1,2,5-oxadiazole (5a) have NQCC which are very similar both in magnitude and direction [1] to those for either hydroxylamine (22) [51], its N-methyl derivative (MeNHOH) [52] or even methoxyamine ($MeONH_2$) [53], although in the last example only IA data have been reported [53]. These observations led us to consider the relationship of other members of the compounds 2a—2d with simple compounds of the type NH_2X; details of computations on NH_2SH (24) for a comparison 2b, and hydrazine (25) and its 1-methyl derivative (26) for comparison with 2c, d, are given in Appendix A.

In order to test the effect of a trans (23) versus a cis (27) orientation, both were computed and the differences found to be small (Table 3). Thus the close relationship between the NQCC observed between isoxazole (2b) and hydroxylamine (26, 27) was born out by the calculations. A similar close relationship was found between those for isothiazole (2c) and thiohydroxylamine (24).

The position at NH of pyrazole (2c) is more complex owing to the planarity of the environment and the consequential changes in bond angles etc. At *N*−2 however, the relationship with hydrazine is immediately apparent, both in magnitudes and direction. Thus the largest coupling (χ_R of 2c, χ_{zz} of 25) is of similar magnitude, etc. In order that these comparisons can be made, χ_π of the cyclic systems (2b, c) has to be correlated with χ_{bb} (χ_{yy}) of 23 etc.; the other correlations of χ_R and χ_T are obvious in all cases; The similarity of the directions of these PA relative to the bonded atoms is seen by reference to Fig. 1 (for 2a, b, c) and 23, 24b, 25b.

5. Comparison of the Azines and Azoles with Aliphatic Imines

5(a) *Imine Nitrogen*

Although values of NQCC in the PA system are known for pyridine (10) and pyridazine (11) from MW data (Table 3), the non-polar nature of pyrazine (13) and tetrazine (14) leads to no MW spectrum, while the data for pyrimidine (12) is only known in the IA system. In the last instance (12) we obtained reasonably good agreement with the IA data, and hence can use the calculated PA data for comparison with the other azines. We note in passing that the non-zero off diagonal element χ_{ab} for pyrimidine (12) is calculated to be particularly large (−2.60 MHz) and of similar magnitude to χ_{aa} (−2.57 MHz) (Table 3). In order to estimate the accuracy of the computed values for pyrazine (13), we observe that the calculated and NQR values differ by an average of 0.3 MHz for 10—13, and that this is indicative of satisfactory calculated values for pyrazine (13).

If we adopt the above values (MHz) for χ_LP, χ_π and χ_T of −5.1, +3.2 and 1.9 for the isolated imine group (C=N—C), it is clear that χ_π in the azines (10—14) is similar, but possibly slightly larger on average. On the other hand, both $|\chi_\mathrm{R}|$ and $|\chi_\mathrm{T}|$ are much reduced in 10, 11 and 13. The presence of a second N atom in 11—13, leads to a rather variable effect upon $|\chi_\mathrm{R}|$, but it is apparent that it is significantly raised by an adjacent N-atom (11).

In the 5-membered rings (2—9), the value of χ_π at N in the group —CH—N=CH— is always lower than the aliphatic ones, as is shown for 3a—3c (~ +2.4 MHz); the presence of a more electronegative group in a position adjacent to N, as in X—N=CH (X=—NH, —O, —S or —N=CH) leads to a more marked decrease from the aliphatic value. The effect varies with the electronegativity of X, as is shown by the series 2a (χ_π 0.02), 2c (0.79) and 2b (1.37 MHz) with further data from 4a, b and 5a, b. In all cases of 2—9, the value of $|\chi_R|$ is reduced relative to the acyclic case, and this is only partly restored by insertion of a more electronegative centre adjacent to *N* (Table 3). The effects of more distant electronegativity effects can be seen in the results for the 1,2,4-systems (7b, c) at *N*—4. The value of χ_T in the unit C—N=C of the azoles is little different from that of the aliphatic systems (Sect. IVa), but again replacement of C by either —O—, —NH— or =N— leads to an increase.

It is interesting to compare the NQCC for pyridazine (11) with other compounds of the present series containing the NN— bond; if we take the cases with the classical unit C=N—N=C (4a, b) the values for χ_π and χ_T (at either *N*) are 1.78, 3.05 (4a) and 2.11, 2.53 MHz (4b); if we take *N*—3 in the compounds 6b, c containing the unit $—N_3=N_2—X$, we find χ_π and χ_T are 2.19, 2.68 (6c) and 2.98, 2.40 MHz (6b, calculated values). The corresponding values for pyridazine (11), 3.3 and 2.4 MHz, are clearly closer to those of 6b, c. This might indicate that the actual molecule of pyridazine (11) is more close to the Kekulé form having C—N=N—C than that having C=N—N=C. Again these results do not have any relevance to the question of aromaticity, since the closest similarity is between the aliphatic values and the azines (10—13) rather than the azoles (2—9); it is generally conceeded that the azoles are less aromatic than the azines.

5(b) *Secondary (—NH—) and Tertiary (—NMe—) Couplings*

These groupings had no direct parallel in our earlier work [1]. It is clear from the above that planar N-atoms have an intrinsically different set of NQCC from pyramidal ones. This is not just a feature of valency angle at the N atom, since both dimethylamine (19) and pyrrole (1c) have very similar CNC angles (112.2° and 109° respectively), while pyrazole (2c) has CNN 113.1°. All of the couplings at —NH— in these cyclic systems are approximately half those of the aliphatic amines.

If we take the χ_π MW values for the *N*—1 in the series pyrrole (1c), pyrazole (2c) and 1H—1,2,3-triazole (—c), —2.66, —3.02 and —3.86 MHz respectively, we see that the last is very close to that in the nitrosamine 27, and that both have the group —NH—N=X (X=O, N); thus the variation in χ_π in 1c, 2e and 6c seems likely to be a π-donating effect, since electronegativity increases seem to lead to a much smaller negative shift; an example of the latter is χ_π in *N*—2 of 2a (+0.08), 2c (+0.79) and 2b (+1.63 MHz), and all of these values are similar to the corresponding aliphatic compounds (22, 23, 25) where no π-back donation is likely.

The MW structure for pyrazole (2c) shows that the NH group lies 5.2° from R, and towards *N*—2, while the EFG principal axis lies a *further* 23.3° in the same direction [16]. Thus the EFG lies a considerable way from the NH bond axis; the implication of this is that there is no reason to assume [cf. 7, 53] that the LP_N direction is nearly coincident with the EFG *R*-axis in $\geq N$: when a neighbouring N or O atom is present. Indeed, it may well be argued that the *electric field* could lie along the LP_N direction, but that the *field gradient* is maximal away from that axis. It does not seem necessary to postulate that distortion of the LP_N electron pair position at *N*—2 in pyrazole (2c) or 1,2,3-triazole (6c) occurs, owing to the presence of the adjacent (positive) H attached to *N*—1[7, 53]. Indeed, there is evidence to the contrary with adjacent LP_N in the series of 1,3,4-heterocycles (4a—d); here the χ_R are rotated *towards* each-other by ~ 15°, and the same effect occurs, on a slightly smaller scale [18a], in pyridazine (14); lone-pair repulsion would be expected to push the LP_N away from the external bisector, rather than the reverse which is observed. Furthermore, if we compare the LP_N EFG at *N*—2 in the O- and S-compounds (2a, b; 5a, b) we find the rotation towards X (O, S) is larger for O than S; this is the reverse effect to that expected on the grounds of lone pair repulsion.

Both the calculations and the MW data [7] for 1,2,3-triazole (6c) indicate that *N*—1 has its principal axis (χ_R) rotated by an amount very similar to the super-position of that for pyrazole (2c) and imidazole (3c). Whilst both *N*—1 and *N*—3 have χ_R rotated towards their neighbour *N*—2, the latter centre has χ_R rotated towards the NH (or NMe in 6d) rather than towards *N*—3. This same effect was observed with χ_R at *N*—2 in 1,2,3-thiadiazole (6b).

The tetrazoles represent the most complex set of NQCC in the present work, and there is no MW data. The calculations show the largest rotation of χ_R from R occurs at the NH/NMe at $N-1$ in the 1H-series (8a, b); at all the other centres in these molecules the χ_R lie close to the external bisector, but are all displaced in the same direction — towards that of $N-1$. Probably as a result of two adjacent N-atoms, the χ_R at $N-2$ in the 2H-compounds (9a, b) lies close to the bisector R, but the direction is displaced towards the side having more N-atoms. Again χ_R is rotated towards N1 in all the tertiary $\geqq N$: centres.

6. Conclusions

We have found that *ab initio* calculations of double zeta quality give a good agreement with observed MW NQCC, both in magnitude and direction. Although most of the MW results available are in the IA rather than PA systems, we have been able to establish reasonable estimates of PA NQCC for the imine —CH=NH— and planar —NH— groupings. It is clear that conjugation of the latter has a marked decrease in χ_π and this value varies markedly with substitution of ring —CH= by —N=; however, the effect does seem to saturate, and the effect upon the $N-1$ atom is much less in a 1,2,3-triaza system than a 1,2,4-triaza one. The present results suggest that the MW investigation of a number of NMe derivatives (NMe-Series) would be valuable, and that in particular a reinvestigation of N-methyl-pyrrole (1d) is appropriate.

Appendix A. The Computations on Small Molecules

Hydroxylamine (22)

This molecule adopts a trans orientation [51] as the preferred state (22); in order to check that the NQCC are not markedly dependent upon orientation we also carried out an evaluation in the cis orientation, but without any other geometric variation. The total energy results (Table 1) showed the transform to be preferred by 11 Kcal mol^{-1} (47kJ · mol^{-1}), to be compared with previous calculated values of 9.90 [55] and 10.8 Kcal mol^{-1} [56]. The near coincidence of one PA with the NO bond (22) is in agreement with the MW data [51], as is the very high value for η (0.812 calc., 0.993 obs.); in the present work we found χ_R (χ_{LP}) > χ_T (χ_{NO}), whereas experimentally they are equal [51]. The very low value of χ_{yy} (22) was confirmed, and hence the relationship of the hydroxylamine NQCC to those of isoxazole (2a). Previous work on the NQCC [48] yielded χ_{zz} -2.038 a.u., using our value for Q_N this becomes 7.18 MHz (much higher than the present work or the MW results) and η 0.495 (much lower than the present).

Thiohydroxylamine (23)

Although esters of this molecule are known, the free molecule has not been described; the geometry used was based upon 22 and H_2S [57], using an NS length 1.6296 Å from that of the 1,2,5-thiadiazole (5b) [58] with which a comparison of NQCC was desired. The final total energy was markedly lower than previous work (Table 1) [59]. The NQCC follow the same pattern (Table 4) as for those of hydroxylamine (22), except that χ_R is rotated towards the neighbouring atom (S) by 12.2°, a lower value than that for NH_2OH (19.4°).

Hydrazine (24)

This molecule was studied at the gauch conformation observed in the MW structure [60, 61]. The total energy is close to that of previous calculations (Table 1). The NQCC are only known in the IA system [62], with the a-axis almost coincident with the NN-bond axis (cf. the NO-axis in 23); the agreement between these IA results, and the present work is very satisfactory, and lies on the same correlation line as the cyclic systems (Figure 1). A feature of the calculated values in the IA system is the very large off-diagonal element χ_{bc} (+3.260 MHz). In the PA system, the χ_{LP} lies comparatively close to the pyramid axis, and about 14° from the bisector of the NNH angle; it is rotated towards the other N atom, as in the other members of the present series (4, 6); none-the-less χ_{LP} lies close to the HNH symmetry plane, showing that the interaction is largely with the adjacent N-atom rather than the adjacent NH_2 group as a whole. The present work supports the assignment of the principal coupling χ_{zz} (-5.21 MHz calculated) to that lying close to the LP_N axis (i.e. χ_R), with that close to the NN axis as significantly smaller (χ_T $+3.74$ MHz); this supports the contention [62] that χ_{aa} is positive in contrast to earlier work. The present calculated results are in much better agreement with experiment than previous ones [48]. The high values of η in pyrazole (2c) at both N atoms are similar to those in hydrazine (24), and in both cases one PA lies close to the NN axis, with a relatively large magnitude (χ_T in 2c, χ_{NN} in 24); the lower values of χ_π in 2c (to be equated with χ_{LP} in 24) can again be ascribed to the planarity and conjugation of the former.

Methylhydrazine (25a)

The structure used (25b) is that of the inner rotamer observed in the MW spectrum [63], since this is the principal species observed. The computation was carried out in the IA system. The molecule is of direct relevance to the NQCC in the pyrazoles (1c, 1d), but is notable for the fact that quadrupole coupling was only observed at one centre [63] and this was assigned to the NHMe (N1). When the IA values of the NQCC at N1 and N2 are compared with the observed data [63], the assignment of the latter to N1 is confirmed (Table 3). The off-diagonal elements at N1 are significant, (χ_{ab} -0.85, χ_{ac} $+0.03$ and χ_{bc} $+2.86$ MHz), and may be amenable to observation. The calculated EFG principal axes at N1 and N2 lie at about 86° to each-other, and lie close to the LP_N directions as well as the external bisectors of the HNMe and HNH angles respectively; their approximate positions are given by the *c*- and *b*-axes of 24b respectively. However, when seen in the *a*/*b*-projection it is clear that both LP_N are rotated towards each other, by about 10.3° (NH_2) and 13.0° (NHMe) respectively. Each centre has a PA close to the NN bond axis (χ_T) (26). We find χ_{zz} is slightly larger at NHMe (-5.08 MHz) than at NH_2 (-4.71 MHz) in the principal axis frame. The diagonal elements of the IA couplings at NH_2 are particularly small, with the reverse effect upon the off-diagonal terms (χ_{ab} 4.16, χ_{ac} 1.48 and χ_{bc} 1.69 MHz), thus explaining the failure to observe NQCC at the NH_2 site [63].

Vinylamine (21)

The molecule was constructed in the IA system following [47]. The total energy is significantly lower than previous work [70]. The agreement between the calculated and observed [47] IA values of the NQCC is extremely good (Table 3); the only off-diagonal element of any major magnitude is χ_{ac} (1.18 MHz, calc.) corresponding to the pyramidal LP_N position. After allowing for the correlation line between calculated and observed NQCC, the calculated PA values suggest that the expected experimental data will be rather similar in magnitude to that of other similar amines such as Me_2NH [71]. Thus in its pyramidal state, conjugation leads to a negligible change in NQCC for vinylamine.

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