

# **<sup>14</sup>N Nuclear Quadrupole Coupling – Correlation of Experimental and Theoretical Values with Structure\***

Michael H. Palmer

Department of Chemistry, University of Edinburgh, Scotland, U.K.

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*Ab initio* calculations, generally of triple zeta + polarisation quality, and sometimes with configuration interaction and iterative natural orbitals, are reported for a number of N–F, N–Cl and N–O bonded molecules. Evaluation of the electric field gradients (EFG) generally gives a good account of microwave inertial axis data, which can then be extended to the EFG principal axis data.

## **I. Introduction**

In our first two papers on <sup>14</sup>N nuclear quadrupole coupling constants (NQCC,  $\chi_{ij}$ ) [1, 2], we showed that double zeta (DZ) *ab initio* molecular orbital calculations using a Huzinaga/Dunning 9s5p/4s basis [3] gave good linear correlations between the experimental microwave (MW) NQCC and the calculated electric field gradients (EFG,  $q_{ij}$ ) for a range of heterocyclic and other organic molecules.

Fundamental to these studies is a value for the nitrogen atom quadrupole coupling constant ( $Q_N$ ); this is not readily obtained by electronic or microwave spectroscopy, except as the product  $q_{ii}Q_N$ ; however, two relatively recent values have been obtained from scattering experiments; electron scattering yields the value  $17.4 \pm 0.2$  mbarn [4], which is in excellent agreement with both a least squares fit of the data above [2], which yields 17.2 mbarn, and with other theoretical estimates based on small numbers of compounds [5]. However, fast-ion bombardment has yielded  $19.3 \pm 0.8$  mbarn [6] (closer to [5c] than other calculated values), and the error bounds from [5, 6] do not overlap, and clearly do not lead to an agreed experimental value. This discrepancy could be resolved by a marked change in the Sternheimer correction applied in [6]; for the moment we adopt the value 17.2 mbarn and treat it as a scaling factor. Strictly the value will be both

basis set and method dependent, e.g. it could depend upon whether SCF, CI or INO wave-functions are utilised. In general, since we will be concerned with correlations between molecules where the calculations use similar methods, and also with signs and directions as well as magnitudes, this will not be a major restriction.

The basic relationships between the second rank tensors  $\chi_{ij}$  and  $q_{ij}$ , where  $i, j = a, b, c$  if in the inertial axis (IA) system, or  $i, j = x, y, z$  for the principal axis (PA) EFG values, are given in [1]. The relationship of EFG to the *molecular* quadrupole moment tensor  $Q_{ij}$  ( $i, j = x, y, z$ ) is also given in [1];  $Q_{ij}$  are of importance in some non-polar molecules, since experimental values of  $Q_{ij}$  are available from collision broadened MW spectra, and other methods, and hence give an independent check upon the  $q_{ij}$ .

Except where symmetry allows identification of the IA system, the conversion of IA to PA data is often difficult, and not carried out. Hence MW studies often stop at the IA data, which cannot be compared with nuclear quadrupole resonance data (NQR) which are already in the (local crystal) PA system. Fortunately calculations of the present type can be carried out in any desired axis system. We thus record both IA and PA data in some Tables. In most cases we report single molecule calculations, and hence compare with MW data. It is hoped that some of the new IA/PA data will stimulate new experimental MW/NQR work.

## **II. Computational Methods**

Most of the compounds in [1, 2] had relatively low polarity bonds, or at least were well represented

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Reprint requests to Dr. M. H. Palmer, Department of Chemistry, University of Edinburgh, West Main Road, Edinburgh EH9 3JJ.

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by a single canonical form. In the present work we consider rather more strongly interacting groups such as N–Halogen (F, Cl), N–O and cumulative bonded types. The calculations are either DZ or triple zeta with polarization (TZVP); (i.e.  $N$  is represented by 1s, 1s', 2s, 2s' 2s'', 2p 2p' 2p'', 3d<sub>6</sub>–20 functions); where reasonable agreement with experimental data was found or to be expected, the calculations were at the SCF level only. In some cases this was extended to a multi-reference CI basis, and in difficult cases to an iterative natural orbital basis (INO) – that is, the CI wave-function was recycled until the density was static. All computations were carried out in the MW-IA system and the EFG diagonalised to the PA system; in cases where the MW structure was unknown, either a crystal structure was adopted, or the structure was optimised in the DZ or TZVP basis.

### III. Results and Discussion

In general, the total energies (Table 1, a–d) are lower than in any previous work, and selected references are given in the text. <sup>14</sup>N NQCC are given in Tables 2 and 3.

#### 1. Simple symmetric and especially N-halogeno-amines

The symmetric top molecules  $R_3N$  ( $R=F, H, Me$ ) have sharply different NQCC, but relatively similar pyramid angles [7–9]; for the un-symmetrical compounds  $R_{3-x}NH_x$  ( $x=0 \sim 3$ ), the  $R=Me$  series show fairly regular trends [10, 11] in the estimated PA data; we give DZ/TZVP results for  $x=1, 2$  ( $R=Me$ ) (Table 2) for a comparison with MW-IA data.

The PA value for the  $\chi_{LP}$  in  $HNF_2$  (–8.3 MHz) (1) [12] is higher than either  $NF_3$  (–7.07 MHz) [7] or  $NH_3$  (–4.090 MHz) [8], or  $Me_2NH$  (–5.05 MHz) [11]. For both  $HNF_2$  and  $HNMe_2$ , of  $C_S$  symmetry, the bc-plane carries N–H, and the values  $\chi_{bb}$  are relatively small +1.97 ( $HNF_2$ ) and +0.93 MHz ( $HNMe_2$ ) [11, 12]. The markedly different values in  $\chi_{LP(cc)}$  in  $HNF_2$  and  $HNMe_2$  largely reflect the large differences in the  $\chi_{aa}+6.35$  ( $HNF_2$ ) and +3.04 MHz ( $HNMe_2$ ). Although  $HNF_2$  and  $H_2NCl$  are well known,  $H_2NF$  does not seem to be characterised, except by theoretical calculations [13a–c]; these

Table 1. SCF total energies (a.u.) of (a) some simple amines, (b) more complex unsymmetrical molecules, (c) cumulative bonded, and (d) nitrogen oxides.

Molecule	Basis set	Total energy
(a) $MeNH_2$	TZVP	–95.24600
	TZVP	–134.18248
	$NF(^1A)$	–153.72975
	$NH_2F$	–155.02306
	$NHF_2$	–253.84254
	$NF_3$	–352.44574
	$cis-FN=NF$	–307.53365
	$cis-FN=NF$	–307.68776
	gauche- $N_2F_4$	–506.26737
	gauche- $N_2F_4$	–506.48476
	$NF_3$	–352.44574
	$NH_2Cl$	–515.09553
(b) $NH_2NO_2$	$NCl_3$	–1432.83733
	DZ	–259.53141
	DZ	–147.85188
	TZVP	–147.96108
(c) $HNCO$	$CH_2N–CN$	–185.80653
	TZVP	–167.82225
	CI	–168.29467
	TZVP	–490.44793
(d) $NO(^2\pi)$	$MeNCO$	–206.86086
	$HN_3$	–163.89450
	CI	–164.34543
	TZVP	–147.89381
(d) $NO(^2\pi)$	TZVP(GVB)	–129.28147
	CI	–129.67741
	TZVP	–203.98267
	$CI(3M1R)^1$	–204.22854
	TZVP	–204.08920
	$CI(5M1R)^1$	–204.71473
	TZVP(MW) <sup>2</sup>	–258.46194
	TZVP(OPT) <sup>3</sup>	–258.50567
	TZVP(MW) <sup>2</sup>	–333.33521
	TZVP(ED) <sup>2</sup>	–408.16136
	TZVP	–243.74316
	TZVP	–168.88144
	TZVP	–168.90358
	TZVP	–207.95911

<sup>1</sup> 3M1R/5M1R signify 3(5) main (M) reference configurations in a single root (R) CI calculation.

<sup>2</sup> MW/ED are microwave and electron diffraction structures used in the calculations.

<sup>3</sup> OPT signifies SCF optimised structure.

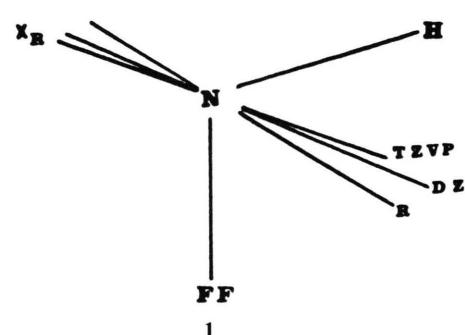


Table 2. Comparison of  $^{14}\text{N}$  nuclear quadrupole coupling constants (MHz) by various methods<sup>1,2,3</sup>.

Compound	N site	Method	Coupling constants (MHz)				Asymmetry parameter	Ref.
			$\chi_{ii}$	$\chi_{ij}$	$\chi_{kk}$	$\chi_{ij}$		
MeNH <sub>2</sub>	N	TZVP(IA)	-3.559 (cc)	1.774 (bb)	1.785 (aa)	1.892 (bc)	0.142	—
		MW(IA)	-4.47 (cc)	2.12 (bb)	2.35 (aa)	—	0.051	[11]
		TZVP(PA)	-4.162 (LP)	2.376	1.786	—	—	—
Me <sub>2</sub> NH	N	TZVP(IA)	-3.404 (cc)	0.846 (bb)	2.526 (aa)	2.731 (bc)	0.494	—
		MW(IA)	-3.97 (cc)	0.93 (bb)	3.04 (aa)	—	0.531	[10]
		TZVP(PA)	-4.714 (LP)	2.188	2.526	—	—	—
		MW(PA)	-5.05 (LP)	2.01	3.04	—	—	[10]
NH <sub>2</sub> F	N	TZVP(IA)	-5.365	5.887	-0.522	-2.149	0.834	—
		TZVP(PA)	-5.761	6.283	-0.522	0	0.834	—
NHF <sub>2</sub>	N	TZVP(IA)	-6.319	0.882	5.437	3.262	0.435	—
		TZVP(PA)	-7.577	2.141	5.437	0	0.435	—
		MW(IA)	-8.32	1.97	6.35	—	—	[12]
NF <sub>3</sub>	N	TZVP(PA)	-6.126	3.063	3.063	0	0	[7]
cis-N <sub>2</sub> F <sub>2</sub>	N	TZVP(IA)	1.351 (cc)	-1.782 (aa)	0.431 (bb)	4.499 (ab)	0.491	—
		TZVP(PA)	1.351	-5.308	3.957	0	0.491	—
		DZ(IA)	0.836	-0.797	-0.040	4.389	0.653	—
		DZ(PA)	0.836	-4.8239	3.9875	0	0.653	—
N <sub>2</sub> F <sub>4</sub>	N	TZVP(IA)	0.120	1.857	-1.977	5.192 (ij) 2.177 (ik) -2.095 (jk)	0.231	—
		TZVP(PA)	-7.218	2.776	4.442	0	0.231	—
NH <sub>2</sub> Cl	N	TZVP(IA)	4.486	0.290	-4.776	-1.170 (ik)	0.882	—
		TZVP(PA)	-4.922	0.290	4.631	0	0.882	—
		MW(IA)	—	—	5.10 (aa)	—	—	[19]
NCl <sub>3</sub>	N	TZVP(PA)	-5.744	2.872	2.872	0	0	—
NH <sub>2</sub> NO <sub>2</sub>	NH <sub>2</sub>	DZ(IA)	-4.952 (cc)	4.310 (aa)	0.642 (bb)	1.628	0.754	—
		DZ(PA)	-5.230	+4.588	+0.642	0	0.754	—
		NO <sub>2</sub>	1.349 (cc)	-0.517 (aa)	-0.833 (bb)	-0.242 (ac)	0.206	—
		DZ(PA)	1.380	-0.548	-0.833	0	0.206	—
NH <sub>2</sub> CN	NH <sub>2</sub>	DZ(IA)	-4.566	2.990	1.576	-1.445	0.348	—
		DZ(PA)	-4.833	3.257	1.576	0	0.348	—
		TZVP(IA)	-3.959	2.537	1.421	-1.263	0.323	—
		TZVP(PA)	-4.196	2.774	1.421	0	0.323	—
		MW(IA)	-4.90 (cc)	3.05 (aa)	1.85 (bb)	—	0.245	[24]
	CN	DZ(IA)	-0.403	-1.828	2.231	0.021	—	—
		DZ(PA)	-0.402	-1.829	2.231	0	—	—
		TZVP(IA)	0.263	-2.943	2.680	0.0821	0.820	—
		TZVP(PA)	0.265	-2.945	2.680	0	0.820	—
		MW(IA)	0.44 (cc)	-3.30 (aa)	2.86 (cc)	—	0.733	[24]
HONO (cis)	N	TZVP(IA)	1.48 (aa)	-5.79 (bb)	4.32 (cc)	1.32 (ab)	0.518	—
		MW(IA)	2.05 (aa)	-5.83 (bb)	3.78 (cc)	—	0.297	[47]
		TZVP(PA)	1.71 (T)	-6.027 (R)	4.317 ( $\pi$ )	—	0.518	—
HONO (trans)	N	TZVP(IA)	1.495 (aa)	-5.261 (bb)	3.766 (cc)	1.809 (ab)	0.432	—
		MW(IA)	1.73 (aa)	-5.28 (bb)	3.55 (cc)	—	0.345	[47]
		TZVP(PA)	1.949 (T)	-5.715 (R)	3.766 ( $\pi$ )	—	0.432	—
HNCO	N	TZVP(IA)	1.684 (aa)	-0.673 (bb)	-1.011 (cc)	—	0.201	—
		MW(IA)	2.056 (aa)	-0.473 (bb)	-1.583 (cc)	—	0.540	[32, 33]
		TZVP(PA)	2.044 (T)	-1.033 (R)	-1.011 ( $\pi$ )	—	0.201	—
MeNCO	N	TZVP(IA)	2.211 (aa)	-1.269 (bb)	-0.941 (cc)	-1.737	0.148	—
		MW(IA)	2.3, 2.86 (aa)	—	—	—	—	[31, 36]
		TZVP(PA)	2.211 (T)	-1.269 (R)	-0.941 ( $\pi$ )	—	—	—
HNO <sub>3</sub>	N	TZVP(IA)	0.234 (aa)	-1.837 (bb)	1.603 (cc)	—	0.745	—
		MW(IA)	0.93 (aa)	-0.82 (bb)	—	—	—	[48]
		TZVP(PA)	0.401 (R)	-2.004 (T)	1.603 ( $\pi$ )	—	0.745	—

Table 2 (continued)

Compound	N site	Method	Coupling constants (MHz)				Asym- metry parameter	Ref.
			$\chi_{ii}$	$\chi_{jj}$	$c_{kk}$	$\chi_{ij}$		
$\text{CH}_2\text{N}_2$	$\text{N}(\text{CH}_2)$	TZVP	-1.687 (aa)	0.076 (bb)	1.611 (cc)	-	0.910	-
		MW	-1.19 (aa)	1.04 (bb)	0.15 (cc)	-	0.748	[43]
	$\text{N}(\text{N})$	TZVP	-2.009 (aa)	5.150 (bb)	-3.141 (cc)	-	0.220	-
		MW	-1.73 (aa)	5.15 (bb)	-3.42 (cc)	-	0.328	[43]
$\text{NO}_2\text{--NO}_2$	N	TZVP	1.838 (zz)	-1.569 (yy)	-0.269 (cc)	0	0.708	-
$\text{NO--NO}_2$	NO	TZVP(IA)	1.085 (aa)	-4.359	3.274 (cc)	2.074 (ab)	0.294	-
		TZVP(IA)	-1.847 (aa)	-1.013 (bb)	2.860 (cc)	-0.501 (ab)	0.455	-
	NO <sup>+</sup>	TZVP(PA)	-5.059 (R)	1.786 (T)	3.274 ( $\pi$ )	0	0.294	-
		TZVP(PA)	-2.081 (R)	-0.779 (T)	2.860 ( $\pi$ )	0	0.455	-
	NO <sub>2</sub>	MW(IA)	-1.9 (aa)	1.6 (bb)	0.3 (cc)	-	0.684	[59]
		MW(IA)	-1.7766 (aa)	0.0585 (bb)	1.7181 (cc)	-	0.934	[58]
	NO <sub>2</sub>	MW(IA)	-2.0 (aa)	0.1 (bb)	-	-	-	[59]
		MW(IA)	-0.526 (aa)	-4.194 (bb)	4.720 (cc)	-	0.777	[58]
NO-NO(MW)	N	TZVP(IA)	-1.818 (aa)	-3.309 (bb)	5.127 (cc)	0.939	0.468	-
		TZVP(PA)	-1.364	-3.763 (R)	5.127 ( $\pi$ )	0	0.468	-
		MW(IA)	-2.242 (bb)	-4.065 (aa)	6.308 (cc)	-	0.289	[62, 63]
NO-NO(SCF)	N	TZVP(IA)	0.215 (aa)	-4.215 (bb)	4.430 (cc)	1.919 (ab)	0.776	-
		TZVP(PA)	0.557 (T)	-4.987 (R)	4.430 ( $\pi$ )	0	0.776	-
MeNO	N	TZVP(IA)	0.329 (aa)	5.811 (bb)	5.482 (cc)	1.126	0.887	-
		MW(IA)	0.50 (aa)	-6.016 (bb)	5.518 (cc)	-	0.834	[69]
		TZVP(PA)	0.528 (T)	-6.011 (R)	5.482 ( $\pi$ )	0	0.887	-
MeNO <sub>2</sub>	N	TZVP	-1.924	-0.705	2.629	0	0.464	-
		MW	-1.18	0.30	0.88	-	0.492	[45]
CH <sub>2</sub> =NOH	N	TZVP	2.384 (aa)	-4.131	1.747	3.718	0.319	-
		MW	3.0	-4.65	1.65	-	0.290	[70]
HN <sub>3</sub>	N, H	TZVP(IA)	4.249	-1.653	-2.596	-1.346	0.160	-
		MW(IA)	4.763	-	-	-	-	[42]
		CI(PA)	4.175 (T)	-1.414	-2.761	0	0.323	-
		N <sub>2</sub>	TZVP(IA)	-0.696	0.897	-0.184	0.386	0.571
	N <sub>3</sub>	CI(PA)	0.264 (R)	-0.684 (T)	0.420 ( $\pi$ )	0	0.228	-
		TZVP(IA)	2.708	-1.950	-0.758	0.203	0.926	-
		CI(PA)	2.391 (T)	-0.604 (R)	-1.787 ( $\pi$ )	0	0.495	-
		MW(IA)	-	-1.35	-	-	-	[42]

<sup>1</sup> Inertial and principal axis (IA, PA) nuclear quadrupole coupling constant axes are defined in the text or in the structures **1** to **27** shown.

<sup>2</sup>  $\chi_{LP}$  refers to a principal axis close to the expected lone pair (LP) direction.

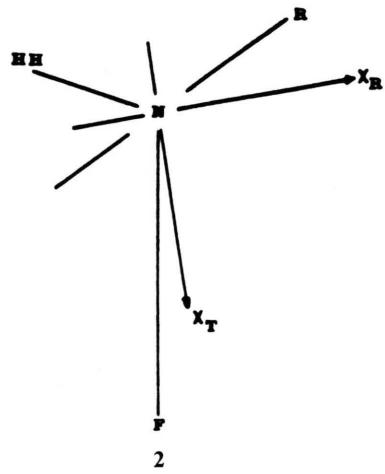
<sup>3</sup>  $\chi_T$ ,  $\chi_R$  and  $\chi_\pi$  for planar systems are used in the sense of References 1 and 2, and refer to tangential, radial and  $\pi$  directions in either cyclic systems or in other molecules where the X-N-Y angle is bisected internally by R with T tangential.  $\chi_R$  and  $\chi_T$  are also shown in most structures **1** to **27**, where the relationship to the inertial axes (a, b, c) are also shown.

seem to predict the NF bond (1.43 Å) longer than either  $\text{NF}_3$  (1.365 Å) [7] or  $\text{HNF}_2$  (1.40 Å), but a rather similar HNF angle [13]. The present calculations on  $\text{HNF}_2$  used the data from [13b]. The values obtained for both  $\text{NF}_3$  and  $\text{HNF}_2$  reproduce the main features of the MW data (Table 2), but all the values are numerically low by about 1 MHz. The reason for this is not clear, but it seems possible that these highly polar molecules may require a CI study, since at an SCF level there is certainly plenty of variational freedom, and the difference between

the DZ and TZVP calculations is really very small, both in magnitudes and directions. For both molecules the  $\chi_{LP}$  is rotated away from the external bisector of the pyramid angle, and towards the adjacent F-atom(s), the effect being similar in the two molecules. The high positive value of  $\chi_{aa}$  in  $\text{HNF}_2$ , parallel to the F-F axis is well reproduced, as is the low value in the N-H plane ( $\chi_T$ ), cf.  $\text{Me}_2\text{NH}$  above. The degree of rotation of  $\chi_R/\chi_T$  is such that with  $\text{NH}_2\text{F}$ , the  $\chi_T$  lies relatively close to the N-F bond. The value of  $\chi_T$  here (+ 6.283 MHz)

Table 3.  $^{14}\text{N}$  NQCC for  $\text{N}_2\text{O}$  (MHz).

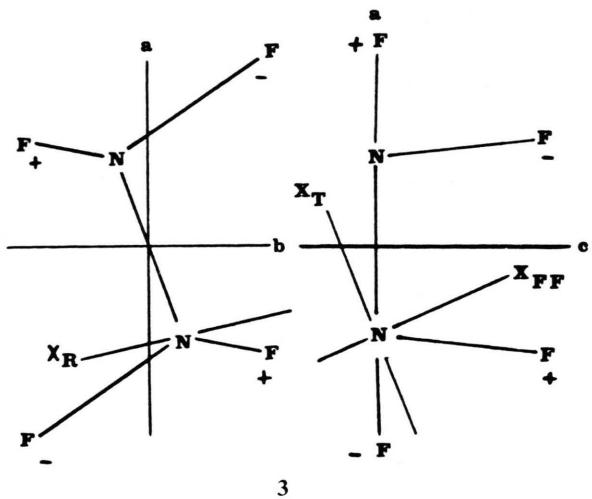
	N (centre)	N (end)	
(a) Experimental			
Microwave [2]	-0.238	-0.792	
Electric resonance [4]	-0.26758	-0.77376	
Beam maser [3]	-0.2694	-0.7767	
(b) Calculated at MW $r_s$ structure (TZ)			
	N (C)	N (E)	Energy (au)
SCF	-1.546	-1.202	-183.73539
CI-IM (valence e)	-1.345	-1.090	-184.14531
CI-5M (valence e)	-0.953	-0.877	-184.15451
CI-5M (all e)	-0.842	-0.898	-184.32831
(c) Calculated at (TZ) $r_e$ structure			
	N (C)	N (E)	Energy (au)
SCF	-1.501	-1.650	-183.74202
INO-1	-0.727	-1.106	-184.16691
INO-2	-0.528	-1.089	-184.16089
INO-3 (mult. ref.)	-0.2823	-0.9639	-184.15658
INO-4	-0.2992	-0.9782	-184.15431



2

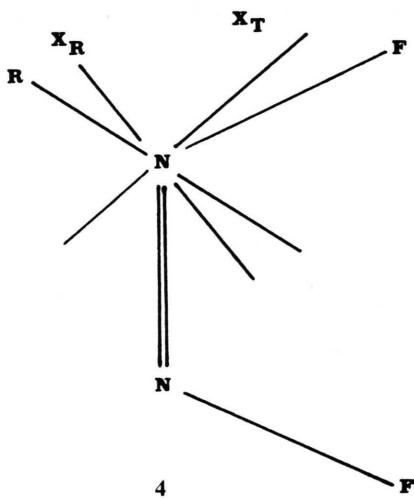
is similar to the  $\chi_{\pi}$  value (parallel to the F-F axis) in  $\text{NHF}_2$ . The lower value of  $\chi_{LP}$  in  $\text{NH}_2\text{F}$  (2) than in  $\text{NHF}_2$  then reflects the replacement of one H by two H atoms. In summary for this group of molecules, a high  $\chi_{ii}$  parallel to an F-F axis (*not* bonded) is the characteristic feature, and this is seen by comparison with other N-F compounds (Table 2). In practice N-F ( $^1\text{A}$ ) has  $\chi_{zz} + 4.1$  MHz [14], but a more relevant example to  $\text{NHF}_2$  and  $\text{H}_2\text{NF}$  is  $\text{NF}_2$  ( $^2\text{B}_1$ ) [15]; this has a high positive  $\chi_{aa} + 5.59$  MHz parallel to the F-F axis.

Both electron diffraction [16] and MW spectroscopy [17] suggest that  $\text{NF}_2-\text{NF}_2$  has a gauche orientation



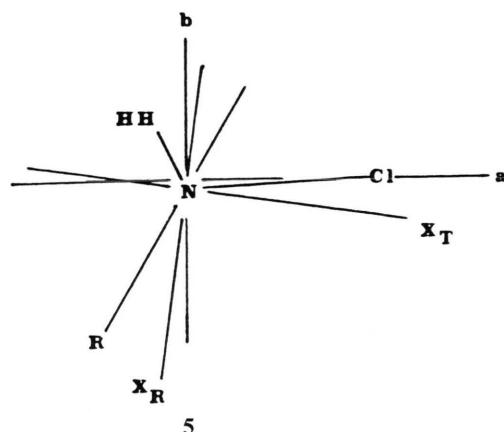
3

with a dihedral angle of  $65^\circ$  (3) [17]. No NQCC was observed [16], although the preceding discussion suggests that the PA values could be high. Under the relatively low resolution conditions used [17], the absence of  $^{14}\text{N}$  NQCC is attributable to the low IA diagonal values ( $\chi_{ii}$ ), where the present work suggests (Table 2) that the off-diagonal elements  $\chi_{ij}$  are all larger in magnitude than  $\chi_{ii}$ . Diagonalisation to yield  $\chi_{zz} - 7.218$  (LP),  $\chi_{yy} + 4.442$  (parallel to F-F) and  $\chi_{xx} + 2.776$  MHz (about  $22^\circ$  from the N-N axis) shows the comparison with the  $\text{NH}_x\text{F}_{3-x}$  series. It is also notable that cis-F-N=N-F gave no observable  $^{14}\text{N}$  NQCC [18] indicating  $|\chi_{aa}| < 2$  MHz. Again we find the off-diagonal element  $\chi_{ab} + 4.49$  MHz is the largest IA value. The EFG-PA values (4) show  $\chi_{LP}$  smaller

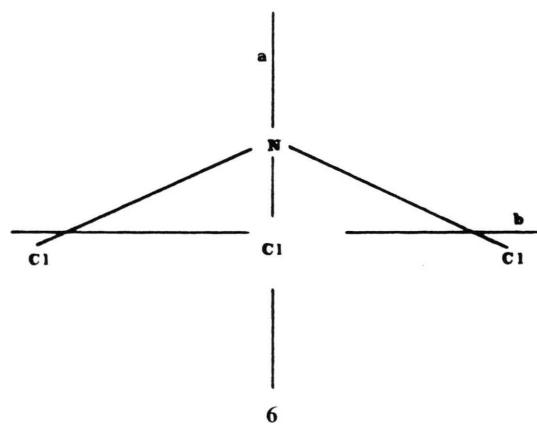


4

(-5.308 MHz) than those for either  $\text{NF}_3$  or  $\text{NHF}_2$  (above), and the direction distorted towards F rather than N. This is consistent with all our previous studies with CH/N/O compounds [1, 2], where  $\chi_{\text{LP}}$  is rotated towards the more electronegative centre. The tangential value  $\chi_{\text{T}}$  of cis- $\text{F}_2\text{N}_2$  is again large and positive (+3.957 MHz). There are much less data on N-chloro-amines, although  $^{35}\text{Cl}$  coupling has been extracted from the MW spectra of  $\text{NH}_2\text{Cl}$  [19] and  $\text{NCl}_3$  [20]. The present TZVP results for  $\text{NH}_2\text{Cl}$  (5) yield a lower energy by about



0.1 a.u. (262 kJ mol<sup>-1</sup>) than a previous DZ study [21], but a slightly poorer IA  $\chi_{aa}$  value (+4.487 MHz) when compared with 5.23 MHz [21] or experiment. There is evidence for  $\text{NF}_3/\text{Me}_2\text{NH}/\text{MeNH}_2$  that the TZVP basis produces lower  $\chi_{ij}$  when used in conjunction with the  $Q_N$  from DZ studies. Direct comparison of the TZVP data for  $\text{NF}_3$  and  $\text{NCl}_3$  (6)



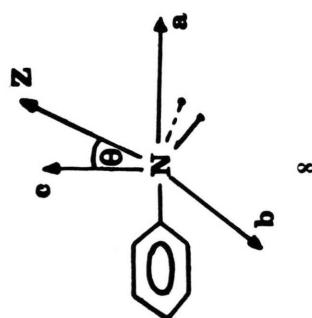
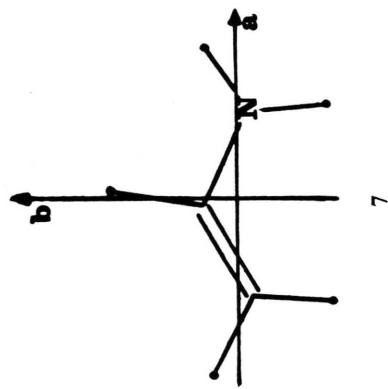
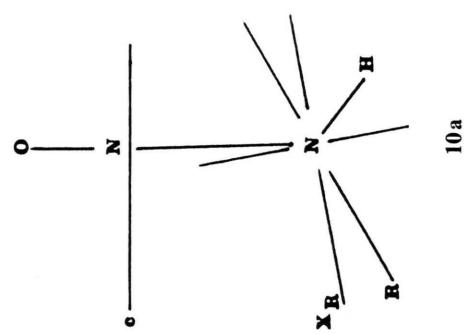
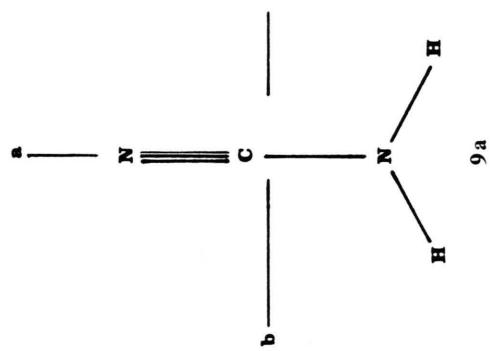
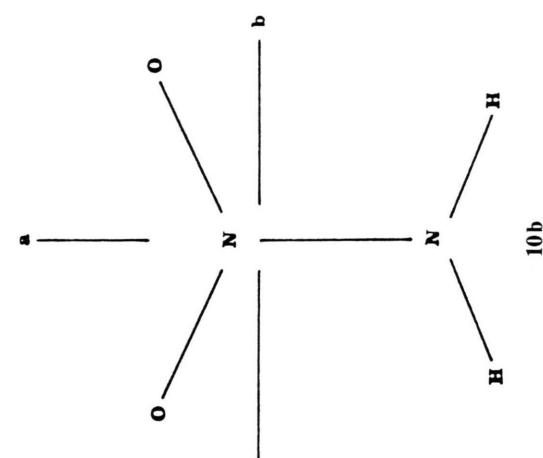
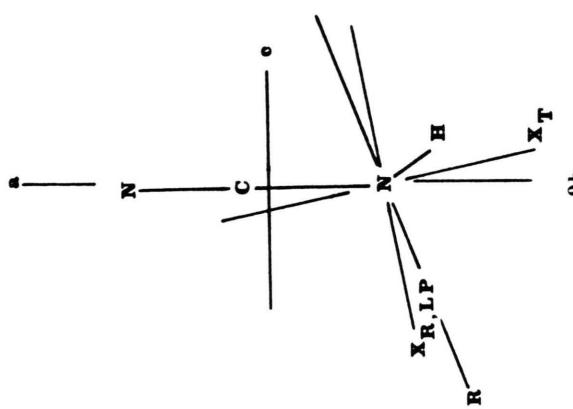
suggests that the experimental value for  $\text{NCl}_3$  should be about 0.5 MHz smaller than that for  $\text{NF}_3$ , and probably near -6.5 MHz. Further MW studies on these chloro- and fluoro-compounds seem worthwhile.

## 2. Further observations on conjugated $^{14}\text{N}$ compounds

We noted previously [2] that changes in pyramid angle and conjugation in vinylamine (7) and aniline (8) relative to methylamine probably lead to opposing effects on  $\chi_{\pi}/\chi_{\text{LP}}$ , and that overall, the conjugation effect in aniline must amount to about 2 MHz. It was thus of interest to compare the calculated PA data with cyanamide (9) [22] and nitramide (10) [23], both of which have non-planar structures (the pyramid angle between the N-N/N-C bond and the  $\text{H}_2\text{N}$  plane is 142° and 128°, respectively, to be compared with 141° and 146° in (8) and (7), respectively).

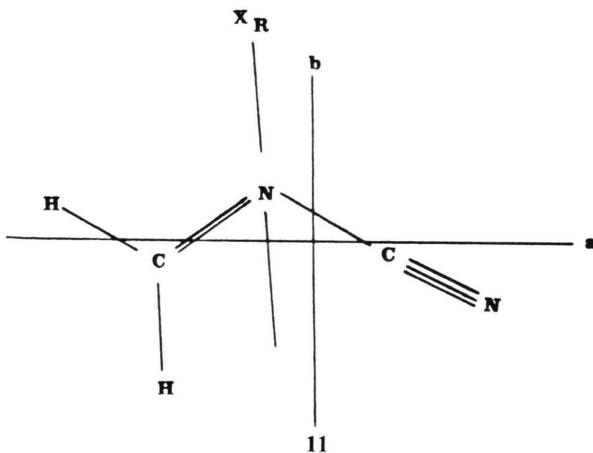
The low resolution of the nitramide study (~3 MHz) led to no observed NQCC [23]. The present DZ values are relatively small at the  $\text{NO}_2$  (10) group (Table 3), and this is discussed in the N-O bonded section. The value of  $\chi_{\text{CC}} - 4.95$  MHz at the  $\text{NH}_2$  group is close to the diagonalised value  $\chi_{\text{LP}} - 5.23$  MHz; both these values seem higher than those expected in aniline or vinylamine, and this together with the more pyramidal character of  $\text{NH}_2\text{NO}_2$  suggests that the conjugation is rather less than in these other compounds. None-the-less the two EFG on the adjacent N atoms do interact, since  $\chi_{\text{LP}}^{\text{NH}_2}$  is rotated about 20° towards the adjacent  $\text{NO}_2$  group. It is interesting to note that the effect lies between the two values (26.0 and 15.5°) at N(1) and N(2) respectively in pyrazole [2]; the latter also contains the NH-N system, but there we are referring to in-plane, i.e. not  $\pi$ -electron NQCC.

The heavy atom skeleton of cyanamide is effectively linear and lies parallel to the  $a$ -axis (9). The  $\chi_{\text{LP}}$  value for the  $\text{NH}_2$  group shows differences between the DZ and TZVP calculations; however, the PA value is probably similar to that of vinylamine, indicating extensive conjugation (see below). Double zeta calculations are notorious with linear molecules. In the present molecule, the CN group is a further good example; thus the axial CN  $\chi_{\text{LP}}$  is the principal  $\chi_{aa}$  value experimentally [24]; the DZ correctly obtains a wide split of the degenerate levels in HCN, but not only gives the wrong sign for



the smallest value, but gives the wrong direction for  $\chi_{zz}$ . This is overcome by the TZVP calculation. The marked difference between the two values  $\chi_{bb}$  and  $\chi_{cc}$  at CN is a strong indicator of the level of conjugation with the  $\text{NH}_2$  group.

The hypothetical condensation reaction of cyanamide with formaldehyde leads to the related conjugated system  $\text{CH}_2\text{NCN}$  [25]; this is the aza derivative of acrylonitrile, and the conjugation in the planar systems is now  $\pi-\pi$  rather than  $\text{LP}_N-\pi$  in  $\text{NH}_2\text{CN}$ , and the  $\text{LP}_N$  of the methyleneimine now lies in the plane. The  $^{14}\text{N}$  NQCC in  $\text{CH}_2\text{NCN}$  were extracted by comparison with *ab initio* calculations [26] and also with acrylonitrile. The difficulties of such analyses of two or more non-equivalent N-atoms were clearly noted (see also [27]); furthermore, the analogy with acrylonitrile broke down owing to a switch of axis, and the calculations [26] gave the wrong order of the IA data. The  $\text{CH}_2=\text{N}-\text{C}$  group lies very close to the EFG-PA axis (**11**) [26], and the experimental value of  $\chi_{bb}$  is

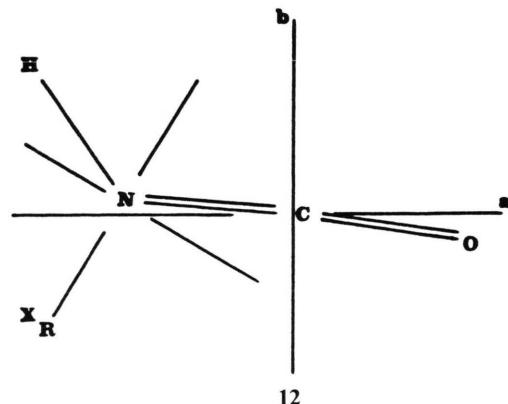


thus effectively  $\chi_{LP}$ ; the value is very similar to other imines (see [2], Figs. 15 and 16), so that it seems likely that relatively little delocalisation of the  $\text{LP}_N$  into the CN in-plane  $\pi(q)$ -bond occurs.

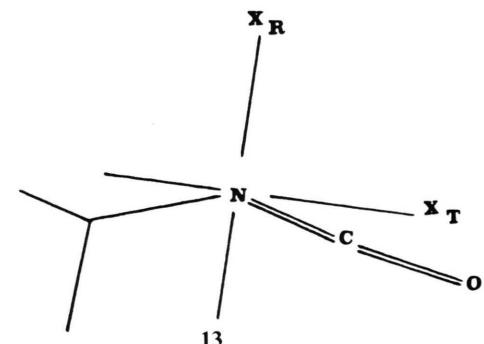
### 3. Cumulative bonded molecules

a) **R-N=C=X.** Contrary to elementary MO theories the cumulative bonded system is not linear; for example HNCO has  $\langle\text{NCO}\rangle$  near  $172^\circ$  with  $\langle\text{HNC}\rangle$  near  $124^\circ$  [28, 29]. Methyl isocyanate ( $\text{R}=\text{Me}$ ,  $\text{X}=\text{O}$ ) is a typical case of a molecule with

large amplitude vibrations, in which the  $\text{Me}-\text{N}-\text{C}$  angle readily deforms [30, 31]; it was thus of some interest to optimise the structures of these molecules, to see whether the equilibrium values were close to spectroscopic values. The results using the TZVP basis are very impressive, with the MeNCO "floppy" angle  $\text{Me}-\text{N}-\text{C}$   $145.8^\circ$  close to the best estimate of  $140.2^\circ$  [30]. All of the molecules  $\text{R}-\text{NCX}$  ( $\text{R}=\text{H, Me}$ ;  $\text{X}=\text{O, S}$ ) have the characteristic a-axis fairly close to the NCX average axis; further the  $\chi_{aa}$  are small and positive (HNCO) [32, 33], (HNCS) [34, 35] (MeNCO) [31, 36]. This even extends to the Cl-NCO case [37], where the a-axis is further displaced from NCO. The results of the TZVP calculations (**12**) (and expt) for HNCO [33]

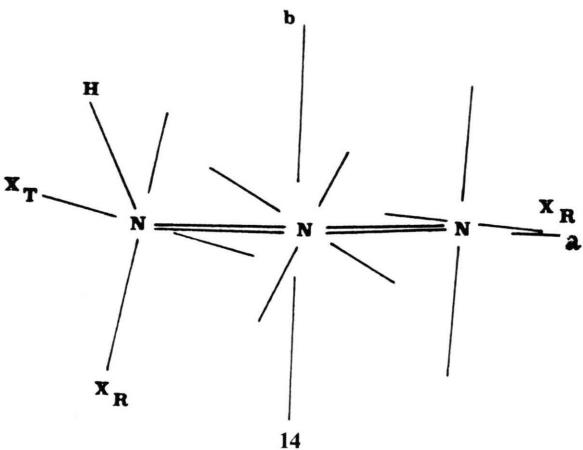


give  $\chi_{aa} + 1.684$  (2.056),  $\chi_{bb} - 0.673$  ( $-0.473$ ),  $\chi_{cc}$  (o.o.p.)  $-1.011$  ( $-1.5583$ ) MHz, which is at the computed equilibrium geometry rather than the MW one. Clearly the errors are relatively small. With "floppy" molecules there is some question of what the observed  $\chi_{ii}$  mean; if we take the observed MW data for MeNCO and compare with computed equilibrium geometry TZVP data, we again do find satisfactory agreement (**13**) as follows with the



single MW value of  $\chi_{aa} + 2.21 (+ 2.86)$  MHz. The principal EFG axis data provide a more meaningful comparison for HNCO and MeNCO; the  $\chi_R$  corresponding to  $\chi_{LP}$  rather closely in direction, are singularly small ( $-1.033$  and  $-1.270$  MHz respectively), with  $\chi_T$  and  $\chi_\pi$  also having small and comparable values between the pair of compounds. Thus although the HNC and MeNC bond angles are very different, the PA-EFG are very similar.

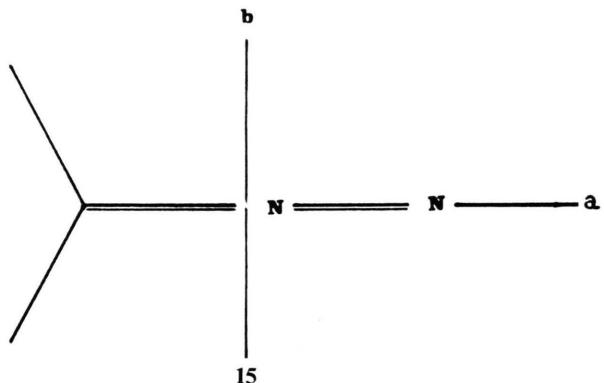
b) **Hydrogen azide and diazomethane.** The structure for  $\text{HN}_3$  was optimised, and the largest TZVP basis set yielded  $\text{HN}_1$  1.004,  $\text{N}_1\text{N}_2$  1.235,  $\text{N}_2\text{N}_3$  1.089 Å,  $\langle \text{HN}_1\text{N}_2 \rangle$  108.5°,  $\langle \text{N}_1\text{N}_2\text{N}_3 \rangle$  173.7°, again showing the non-linear cumulative skeleton. The experimental equilibrium structure of  $\text{HN}_3$  is still not known, but the earlier MW assumption [38, 39] of NNN linearity is no longer assumed [39, 40], and the values obtained here must be close to the experimental values; all the bonds are slightly smaller than previous large basis calculations [41]. Only two NQCC have been positively identified [42] for  $\text{HN}_3$ ,  $\chi_{aa}$  at the two end N-atoms ( $+4.85$  MHz at  $\text{N}_1\text{H}$ ,  $-1.35$  MHz at  $\text{N}_3$ ). The present TZVP optimum structure values are about 1 MHz low at both centres. The EFG-PA value at  $\text{N}_1\text{H}$  lies relatively close to the external bisector (14) (R) of



the  $\text{HN}_1\text{N}_2$  angle as expected; both  $\chi_R$  and  $\chi_\pi$  are nearly double those in HNCO, and this can be attributed to the differential polarity of the neighbours to  $\text{N}_1$ , i.e.  $\text{H}+\text{C}$  versus  $\text{H}+\text{N}$ , and their effect upon  $\chi_T$  (+2.044 MHz for HNCO and +4.542 MHz for  $\text{HN}_3$ ). Extensive CI leads to little change in  $\chi_{aa}$  at  $\text{N}_1\text{H}$ , but  $\chi_T$ ,  $\chi_R$  and  $\chi_\pi$  all decrease with an increase in  $\eta$ . The cylindrical symmetry of the azide

ion is missing at the remote atom  $\text{N}_3$  of  $\text{HN}_3$  owing to the distant H-atom, and this is seen by the large differences in the two “ $\pi$ ”-values here called  $\pi$ - and  $q$ - (in-plane  $\pi$ );  $\chi_R$  0.779,  $\chi_q$   $-1.950$  and  $\chi_\pi$   $+2.720$  MHz respectively. The perturbation produced by the H-atom of about 4.6 MHz is very large. As expected on the basis of two N neighbours, NQCC at the central atom  $\text{N}_2$  are very small ( $< 1$  MHz), but just above the values which were thought to be resolvable [42].

The structure of diazomethane  $\text{CH}_2\text{N}_2$  was also optimised in the TZVP basis; the final structure is slightly smaller than the MW one [43]. The NQCC at the terminal N of  $\text{CH}_2\text{N}_2$  are very close to experiment (15), but the values at the central atom

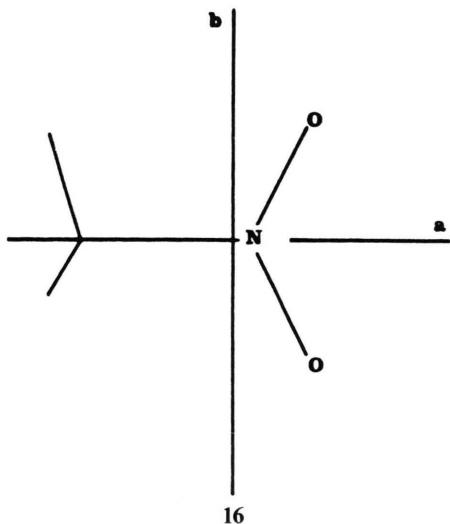


are markedly different in relation to the  $\pi/q$  values. There seems a need for further work on this compound. As with  $\text{HN}_3$ , the difference between the magnitudes of  $\chi_\pi$  and  $\chi_q$  at the terminal N atom is very large – a difference of 8.5 MHz [44].

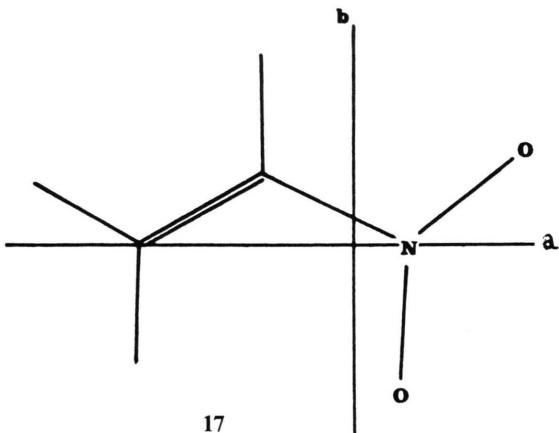
#### 4. The Nitrogen Oxides and Their Derivatives

In this section there is a considerable amount of microwave, inertial axis NQCC data, some of which seems inconsistent with normal values; this may be a result of some unusual bonding situations, e.g. long (weak) bonds, or may disclose non-unique solutions of the NQCC data in the spectral assignments. We start with some straightforward cases; all of the computations here use TZVP bases; in the small molecules, the calculations are at the SCF, CI and iterative natural orbital (INO) levels. Generally these studies are at the microwave structure  $r_s$ ; some have also been optimised to equilibrium structure ( $r_e$ ). The larger cases are at an SCF level unless otherwise stated.

a) **Nitromethane  $\text{CH}_3\text{NO}_2$ .** The local  $C_{3v}$  symmetry of the Me group leads to the IA and PA systems coinciding (**16**). All values are small, and

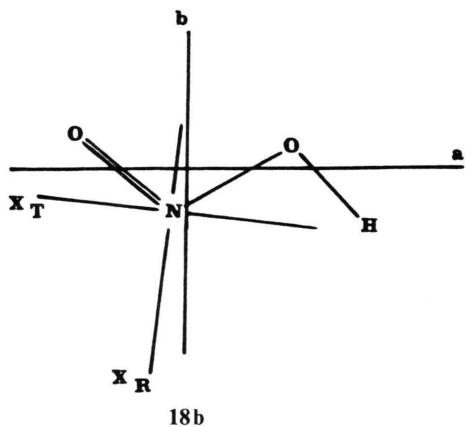
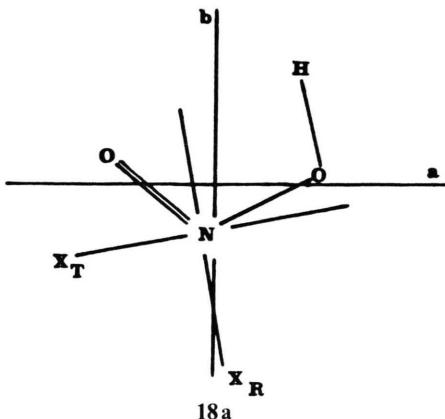


this is generally a problem with  $\text{N}=\text{O}$  bonded compounds, except where  $\text{LP}_N$  occurs; the  $\pi$ -value is positive as is that parallel to the O–O axis ( $\chi_{bb}$ ), leaving the  $\chi_{aa}$  ( $\text{NO}_2$  internal bisector) value negative [45]. Note that  $\chi_{aa}$  and  $\chi_{\pi}$  are similar to those for  $\text{NO}_2$  in  $\text{NH}_2\text{NO}_2$ , but that  $\chi_{bb}$  seems to be opposite in sign. Although the axes are no longer symmetrically placed in nitroethylene (**17**) [46a], it



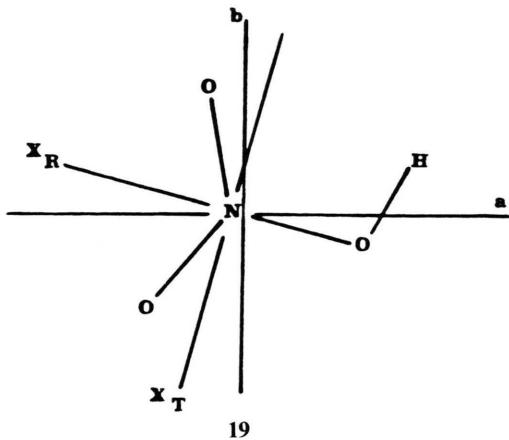
seems clear that the same general pattern of NQCC, both in sign and magnitude occur. However, the very low magnitudes, and high polarity of the molecules may both act to switch axes for  $\chi_{zz}$  in the solid state (see [46 b]) or in suitable substituted cases.

b) **cis and trans Nitrous acids  $\text{HONO}$ .** In both these molecules the  $b$ -axis lies relatively close to the bisector of the O–O angle (**18**), and hence close to



the nominal lone pair [47]. The computed EFG in the IA system lead to NQCC within about  $\pm 0.3$  MHz of the estimated MW ones. Rotation to the principle axis values shows high negative values for  $\chi_R$  and high positive for  $\chi_{\pi}$ ; as expected for two rather similar neighbours to N, although differently bonded,  $\chi_T$  is relatively small (and positive). The calculations suggest that  $\chi_R/\chi_{\pi}$  are slightly larger in magnitude in the *cis*-than the *trans*-isomer.

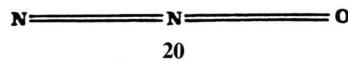
c) **Nitric acid.** Two of the NO groups are locally very similar, and of course the large negative lone pair  $\chi_{LP}$  (equivalent to  $\chi_R$  in HONO) is no longer present. Hence all  $\chi_{\text{HNO}_3}$  are smaller, but  $\chi_{\pi}$  is again positive [48]. The value (**19**) of  $\chi_T$  (relatively close to  $\chi_{bb}$  in direction) has become negative, and this is seen elsewhere in  $\text{XNO}_2$ ;  $\chi_R$  is small and positive, as



expected on the basis of three O attachments, and has some connection with  $\chi_T$  in HONO. The discrepancy between computed and MW values is larger here, but notwithstanding the MW quoted error bounds  $\pm 0.10$  MHz, the text actually notes "the very small splitting" which was only resolved at low temperature.

d) **Nitrous oxide  $\text{N}_2\text{O}$ .** This is the simplest stable molecule with two non-equivalent  $^{14}\text{N}$  nuclei. The microwave  $r_s$  structure shows  $r_{\text{NN}} 1.1286$ ,  $r_{\text{NO}} 1.1876$  Å and linear [49]; although early estimates of the equilibrium lengths suggested 1.136 and 1.186 Å respectively [49], we find the equilibrium structure, at an SCF level and using a TZVP basis to be 1.0826 and 1.1717 Å respectively. Of course at a CI level these shortenings could disappear with  $r_e$  becoming closer to  $r_s$ ; there is some evidence of this below.

The standard MW spectrometer does not resolve more than four out of the seven  $^{14}\text{N}$  splittings [50], whereas all can be obtained by molecular beam maser [51] and electric resonance [52] techniques. The values ( $\chi_{aa}$ ,  $\chi_{zz}$ ) are notably small and negative at both the central and end N atoms (20). SCF



calculations using the TZVP basis (Table 3) at both  $r_s$  and  $r_e$  structure yield values much too large, and the magnitudes differ between the two structures. An all electron CI leads to a common order, and markedly reduces the errors; while the  $r_e$  study gives further improvement in 3 phases of iterative natural orbital (INO-x) refinement, it is interesting that the

5M1R single pass CI on all electrons actually leads to the lowest total energy of the set. This suggests that the true  $r_e$  may lie closer to  $r_s$  than to the SCF  $r_e$ .

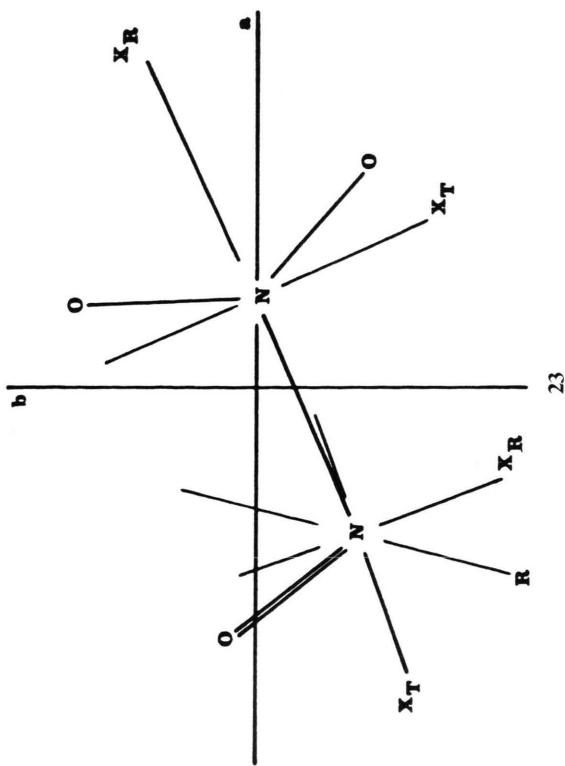
A comparison of the series  $\text{N}=\text{N}=\text{O}$ ,  $\text{N}=\text{N}=\text{NH}$  and  $\text{N}=\text{N}=\text{CH}_2$  shows that as the electronegativity of the substituent (O, NH, CH<sub>2</sub>) decreases the axial coupling  $\chi_{aa}$  at the terminal N shows a negative trend -0.777, -1.35 and -1.73 MHz experimentally; it is clear that the middle N atom shows a similar trend but with lower shift (-0.269,  $\sim -0.8$ , -1.19 MHz respectively).

In conclusion then, it seems clear that MW spectra of polyatomic molecules will often not resolve small NQCC, and that SCF calculations may compute them in the wrong internal order, unless extensive CI is performed.

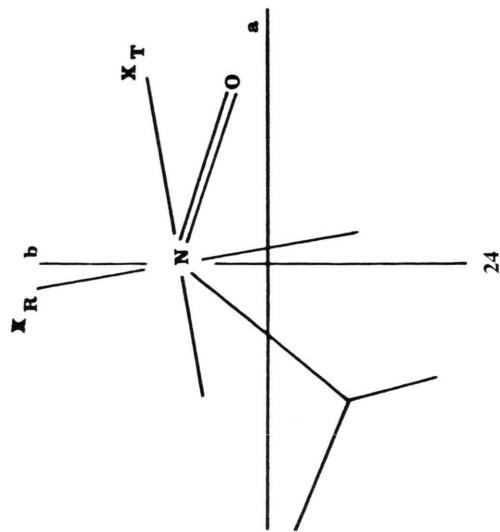
e) **Nitric oxide, nitrogen dioxide and their dimers.** This group of five compounds consists of two radicals  $\cdot\text{NO}$  and  $\cdot\text{NO}_2$  and the three possible dimers. Each of the latter have long N–N bonds and hence can be expected to show difficulties for SCF calculations.

i) **Nitric oxide ( $^2\pi$ ).** The present TZVP SCF calculations were followed by all-electron multi-reference CI, with marked lowering of energy. It is necessary to operate in a generalised valence bond procedure (GVB) to obtain symmetry of the single electron in the two  $\pi$ -orbitals. The  $\chi_{zz}$  at the SCF level -2.335 MHz is still significantly high relative to experiment (-1.85 MHz) [53] but the CI reduced this to -1.62 MHz (previous calculations yielded -2.50 MHz [54]).

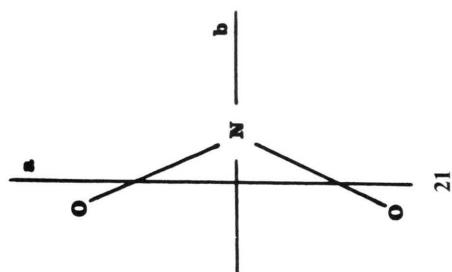
ii) **Nitrogen dioxide ( $^2\text{A}_1$ ).** In practice the SCF procedure initially gave the  $5\pi$ -electron  $^2\text{B}_1$  state; by suitable exchange of orbital occupancy the SCF produced a lower energy  $^2\text{A}_1$  state, and the order of the states was confirmed by multi-reference all-electron CI. Accurate experimental  $^{14}\text{N}$  NQCC for  $\text{NO}_2$  ( $^2\text{A}_1$ ) have proved difficult to obtain, owing to the overlay of various unknown parameters; for instance the values  $\chi_{bb} - 2.57 \pm 0.7$  (symmetry axis),  $\chi_{aa} + 1.75 \pm 1.3$  and  $\chi_{cc} (\pi) + 0.82 \pm 0.6$  MHz were subsequently replaced by  $-1.71 \pm 0.4$ ,  $+0.45 \pm 0.06$  and  $1.26 \pm 0.05$  MHz respectively, i.e. a switch of axis order occurred [55, 66]. At the SCF TZVP level, the NQCC values obtained are all too large, and  $\chi_{aa}$  is of wrong sign; this last point is rectified readily by CI and the INO method, but  $\chi_{bb}$ ,  $\chi_{cc}$  persist at values 50% higher than the experimental ones above. The reason is not clear,



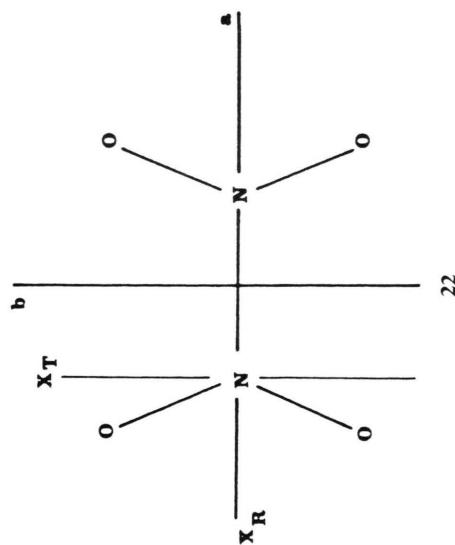
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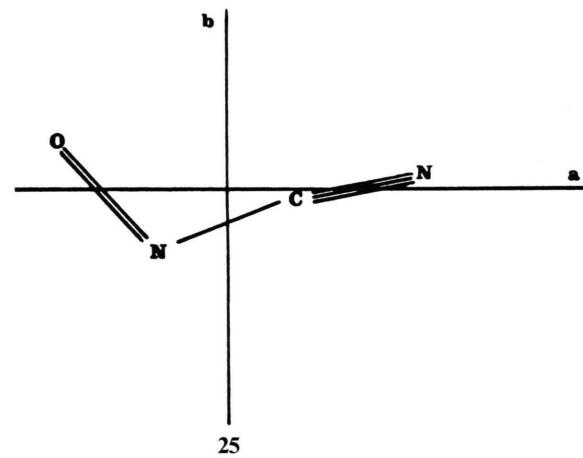


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but one possibility is that the complex  $\text{NO}_2$  spectrum has still not been correctly interpreted. However, the conclusion that  $\chi_{bb}$  ( $\text{C}_2$  axis) (21) is relatively large and negative and  $\chi_{cc}(\pi)$  is positive seems probable on the basis of both  $\text{NO}_2$  and  $\text{MeNO}_2$  and their respectively TZVP calculations. The order on a basis  $|\chi_{zz}| > |\chi_{yy}| > |\chi_{xx}|$  seems less certain for these molecules.

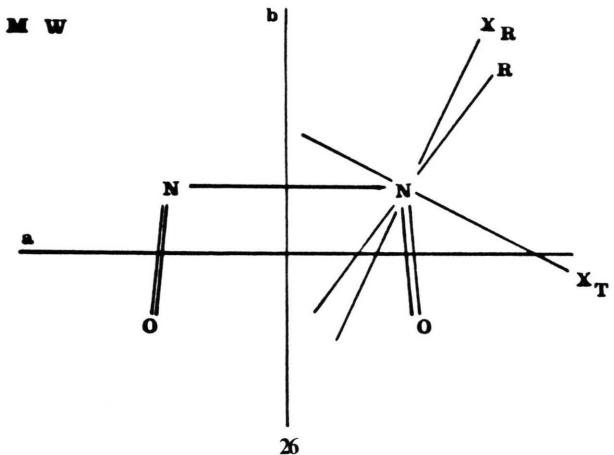
iii) Dinitrogen tetroxide  $\text{N}_2\text{O}_4$ . There is no dipole moment and hence no microwave spectrum for the symmetrical  $^{14}\text{N}$  species. The present TZVP calculations, using the electron diffraction structure [57] at an SCF level only, suggests that  $\chi_\pi$  will again be positive; the balance between  $\chi_{NN}$  and  $\chi_{OO}$  seems uncertain in the light of the section (ii) above, but  $\chi_{NN}$  is probably negative (22).

iv) Dinitrogen trioxide  $\text{NO}_2\text{--NO}$ . There is strongly conflicting experimental information here; the higher resolution data [58] suggests that the  $\text{NO}_2$  group parameters have  $\chi_\pi + 4.72$  MHz, much higher than the present TZVP calculations, which are closer to the earlier (classical) MW study [59]. The values of  $\chi$  at the NO centre in  $\text{N}_2\text{O}_3$  do not seem reasonable in either study; given even weak  $\sigma$ -bonding between  $\cdot\text{NO}$  and  $\cdot\text{NO}_2$ , we would expect some development of a  $\text{LP}_N$  at NO, with large negative coupling lying close to the  $b$ -axis (23); this is not found. The  $\chi_\pi$  at NO in a normal R-NO bonded system is large and positive; for example  $\text{MeNO}$  has  $\chi_{LP}$  (near  $-6.02$ ),  $\chi_\pi + 5.52$  MHz (24) [60], while  $\text{NO--CN}$ , where two  $^{15}\text{N}$  single labelled species were studied has  $\chi_{LP} - 5.68$ ,  $\chi_\pi + 4.16$  MHz [61]; also the orientation of the  $a$ ,  $b$ -axes is similar in  $\text{NO--NO}_2$  and  $\text{NO--CN}$  (25). In the absence of



studies of  $^{15}\text{N}$  single labelled compounds, it is difficult to be confident for  $\text{NO--NO}_2$ ; however, if we re-assign pairs of  $\chi_{aa}/(\chi_{bb} - \chi_{cc})$  [58] we arrive at N(1)  $\chi_{aa} - 0.526$ ,  $\chi_{bb} - 0.567$ ,  $\chi_{cc} + 1.093$  MHz, N(2)  $\chi_{aa} - 1.777$ ,  $\chi_{bb} - 3.569$ ,  $\chi_{cc} + 5.345$  MHz; if these assignments are made N(1) to  $\text{NO}_2$  and N(2) to NO respectively, and the Brittain and Cox data [59] ignored, then the values bear better relationships to all the compounds  $\text{NO}_2$ ,  $\text{MeNO}_2$ ,  $\text{NO--CN}$  etc. The difficulties of correctly assigning the two values of  $\chi_{aa}$  to their respective  $(\chi_{bb} - \chi_{cc})$  in cases of non-equivalent  $^{14}\text{N}$  nuclei were referred to above [25]. Thus the question of whether the revised experimental data [58] represents a unique (and hence correct assignment of the spectrum) remains. If the Kukolich assignments [58] are correct, then the nature of the bonding in  $\text{NO--NO}_2$  becomes very obscure.

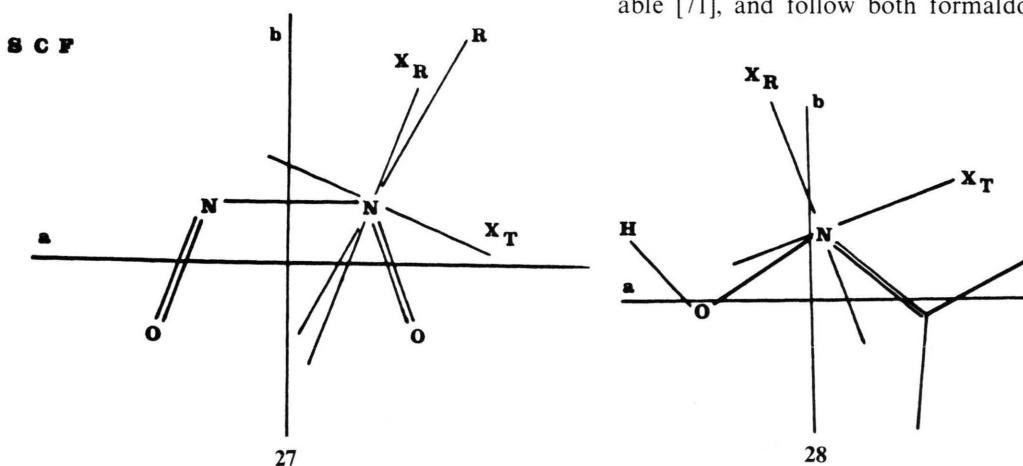
v) Dinitrogen dioxide  $\text{ON--NO}$ . Two investigations have shown that the  $^{14}\text{N}$   $\chi_\pi$  NQCC of this *cis*-dimer are large and positive ( $+6.308$  MHz) [62, 63]. The in-plane values  $\chi_{aa} - 4.065$ ,  $\chi_{bb} - 1.818$  MHz are still indicative of  $\chi_{LP}$ , even though the N-N length is longer (2.236 Å) than either  $\text{NO}_2\text{--NO}_2$  1.782 Å [57] or  $\text{NO--NO}_2$  1.864 Å [59]. The present SCF calculations (TZVP) yield  $\chi_{aa} - 3.309$ ,  $\chi_{bb} - 1.818$  and  $\chi_{cc} + 5.127$  MHz (26) at the



MW geometry. However, the off-diagonal element  $\chi_{ab} + 0.939$  MHz is relatively small in influence and the EFG-PA value  $\chi_R - 3.763$  MHz is certainly smaller than for a normal  $\chi_{LP}$ . There have been a number of previous theoretical studies of  $\text{N}_2\text{O}_2$  [64–68]; most of these have been concerned with

the equilibrium structure at an SCF level [64–67]; we confirm with the TZVP basis, that such studies lead to a smaller molecule than the MW structure. In the present work we obtain  $r_{\text{NN}}$  1.616,  $r_{\text{NO}}$  1.134 Å,  $\langle \text{NNO} \rangle$  110.1; at this geometry, the EFG-PA

factor directly associated with aromatic character in the last instance, since formaldoxime has  $\chi_R$  ( $\chi_{bb}$  lies close to R)  $-4.65$  and  $\chi_\pi$  1.65 MHz [70]; the situation for oximes more generally could be more complex owing to H-bonding, but the values  $-5.96$  MHz ( $\chi_R$ ) and  $4.25$  MHz ( $\chi_T$ ) seem reasonable [71], and follow both formaldoxime (28) and



values give  $\chi_R$  4.987,  $\chi_\pi + 4.430$  MHz, with values more like nitroso and other R-N=X systems. Further CI studies on these N-O compounds are in progress.

#### IV. Conclusions

An important feature with various N-O bonded molecules is that the experimental data is often poor in accuracy, either because the resolution was poor, or the analysis complex owing to other phenomena being superimposed, or more than one non-equivalent N atoms being present. When comparatively straightforward cases arise, such as in nitroso-methane [69], the agreement between TZVP calculated and the MW data re-emerges. In this particular instance,  $\chi_{bb}$  is very close to  $\chi_R$ , the  $\text{LP}_N$  value; the critical point of the analysis however, is that  $\chi_T$  is very small (although the neighbours at N are C+O), while  $\chi_\pi$  is very large. This contrasts with isoxazole, where  $\chi_R$  is similar, but  $\chi_T$  is large and  $\chi_\pi$  very small [1]; indeed, it is not a

isoxazole. Thus the switch of bonds C-N=O to C=N-O leads to quite fundamental effects on the  $^{14}\text{N}$  NQCC.

In our first two papers [1, 2], we showed that a DZ basis gave a good account of  $^{14}\text{N}$  NQCC in 5- and 6-membered ring heterocycles, and a number of small other compounds. When the bonding is more polar, as in N-Halogen and N-O compounds especially N=O types, there are MW experimental problems resulting from low resolution, and it may not be possible to carry out suitable isotopic substitution to obtain enough  $\chi_{ii}$  and  $\chi_{ij}$ . Thus it is difficult to assess the accuracy of the computed data. In order to offset the high polarity, we have generally used a TZVP basis in the present work; the d-type functions on C, N, O may not be optimal for EFG purposes, since they are primarily intended to increase variational flexibility, and reduce the effect of the LCAO approximation. For most purposes, we now regard extensive CI/INO as essential for highly polar bonds if accurate values are required. If broad trends only are necessary SCF DZ and TZVP calculations will generally suffice.

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