Nuclear Quadrupole Coupling Constant assignments for a series of azoles and azines by Hartree-Fock SCF-Cluster and Lattice Calculations*

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We present *ab initio* Hartree-Fock lattice calculations on a series of heterocyclic and other compounds. Some of these have previously been studied by cluster calculations with the same DZ basis sets at the SCF level. The electric field gradients at the nitrogen centres, are related to NQR experimental determinations of nuclear quadrupole coupling constants. The compounds studied include imidazole and pyrazole, 4-nitroimidazole, 4-nitropyrazole, pyrazine, and tetramethylpyrazine, pyridinium chloride, and N-methylpyridinium iodide, and pyridine-N-oxide.

Introduction

Nuclear quadrupole coupling constants (NQCC, χ_{ii}) obtained by microwave spectroscopy (MW) of the vapour, or NQR of the polycrystalline solid, are related to the electric field gradients (EFG, q_{ii}) obtained from electronic wave-functions by

$$q_{zz} = \langle \Psi_0 \mid (3z^2 - r^2)/r^5 \mid \Psi_0 \rangle \qquad (1)$$

and

$$\chi_{ii} = e^2 Q_N q_{ii} / h a_0^3 = 234.96\, Q_N q_{ii}, \qquad (2)$$

where the EFG of a diagonal element $q_{(3z^2-r^2)/r^5}$ is shown together with the proportionality relation. Recently, we reported *ab initio* lattice calculations for a variety of organic and inorganic molecular systems containing ^{14}N centres [1, 2]. These are a refinement of our previous studies on clusters [3 - 5] where a test molecule was surrounded by its nearest shell of neighbours from the crystal lattice. All of these studies use the Hartree-Fock Method and involve all electrons in the system under consideration, and the only empirical factors are the atomic orbital bases, a necessary feature fo all MO calculations.

We present a number of new results using **'CRYSTAL-92'**, which is an *ab initio* Hartree-Fock SCF programme for periodic systems [6 - 8] in particular, we put some of our previous cluster calculations on a more rigorous footing, and then extend the study to some related heterocyclic compounds. EFG calculations of at least a double-zeta (DZ) basis are necessary to obtain reasonable agreement with experimental values of NQCC. Previous work with **'CRYSTAL-92'** and DZ bases generally required the basis to be scaled to higher exponents, to avoid numerical failure of the calculations. A key feature of the present version is the extension of the numerical methodolology to enable basis sets with diffuse (valence type) orbitals to be studied.

1. Methods

1.1. Basis sets

We used Huzinaga/Dunning double zeta(DZ) [9, 10] bases for these lattice calculations, as discussed below. These are comparable with our previous work [3 - 5], and generally give reliable values for both structural features in the single molecule calculations and the NQCC when compared with NQR data. S atoms had a 66-21G [11] for preliminary studies, which was replaced in the final calculations by 10s6p sets from Roos and Siegbahn [12] or 14s10p sets from Huzinaga [13], both contracted to DZ. In some cases, a halide anion present was represented by the Hay and Wadt [14] large core-pseudopotential(ECP); in this basis, the atoms Cl and I are represented by an sp basis of 4,4 and 3,3 GTO's, respectively.

The lowest DZ GTO exponents (a_i) have values 0.2137(O), 0.1654(N) and 0.1146(C), respectively. In a crystal lattice, these lead to eigenvalues of the overlap matrix (S_{ij}) being 10^{-4} or less; when inverting

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Table 1. Cell Energies and Lattice Calculation Details.

Compound	AO's per cell	Cell symmetry	Energy per cell/a.u.
Thioacetamide	400	$P2_1/C$	-4244.20428
Imidazole	232	$P2_1/C$	-898.38279
4-Nitroimidazole	344	$P2_1/C$	-1712.01887
Pyrazole	464	$Pna2_1$	-1796.57602
1-Nitropyrazole	344	$P2_1/C$	-1711.67219
1-Acetylpyrazole	158	molecule	-376.45191
Pyrazine	136	Pmnn	-524.74349
Tetramethylpyrazine	496	Pbca	-1673.03422
Pyridine 2HCl	164	P_{-1}	-553.73333
1-Methylpyridinium iodide	360	$P2_12_12_1$	-1188.34478
Pyridine-N-oxide	320	$C222_1$	-1284.54391

the S_{ij} matrix, numerical problems often arise. This is now overcome by projecting out such eigenvectors, and is a major technical development from our previous work [1, 2], where successful diagonalisation of the Fock matrix was capricious. Some of the calculations, under all circumstances, produced such large files of ('bielectronic') electron repulsion integrals(in excess of 10Gb), that 'direct-scf' calculations were performed; i. e. the Fock matrix was computed directly, without a complete set of integrals being preformed. Since the overall integral set has to be recalculated at each iteration, this makes the calculations much longer in CPU time than conventional SCF methods. A number of other critical features for eventual success with **CRYSTAL-92** are discussed in our previous papers [2]. The principal NQCC results and comparison with experimental data are shown in Tables 1 and 2.

1.2. The ^{14}N Atomic Coupling Constant (Q_N)

In much of our previous ^{14}N work [1 - 5], we treated the value of Q_N as a scaling parameter, using a correlation of EFG (q_{ii}) against χ_{ii} from microwave data to evaluate the appropriate Q_N. This was to enable a series of EFG results to be more easily compared with the experimental NQCC values; the reason for the necessity for such scaling, is the limited size of the basis sets, such as the DZ basis used here. The nuclear term implicit in (1) is constant for a fixed geometry whatever the basis set, whereas the electronic term decreases by about 25% between the DZ value and the limiting SCF value including extensive CI. Since the last procedures are presently impracticable, the DZ basis was essential for this work. The scaled DZ ^{14}N correlation constant was 3.5244 MHz/a.u (15.000 mb); this value is widely used in *ab initio* studies by other workers. In order to facilitate comparison with our earlier ^{14}N studies and make comparison with experiment simple, we again give scaled results; the best current value for Q_N is 20.2mb and is used in one case where we performed molecular calculations with MP2 correlation corrections; the Q_H used here is the recommended value 2.860mb [15]; the general relationships are 1 barn = 10^{-28} m^2 = 100 fm^2.

1.3. Lattice Calculations

The data input to CRYSTAL-92 is the crystallographic space group, unit cell parameters, the asymmetric unit, and the basis set. As in conventional molecular SCF methods, the calculations can be performed in a Gaussian orbital (GTO) basis. This programme computes the electronic wave-function in the reciprocal space of the unit cell system; integration is carried out over a set of cells, until the integrals between the 'origin' and the extremities fall below some preset tolerance, and hence can be ignored. More detail concerning the basic method is given in the papers by Saunders et al. [6 - 8], and our implementation of it in our recent papers on inorganic and organic molecules [1, 2]. The method generates a wave-function which represents the bulk material, rather than just a local environment.

2. Results

Our preference for starting coordinates for the asymmetric units are neutron diffraction structures, since these give CH and NH bond lengths close to single molecule studies. However, in most cases x-ray determined structures are the only ones available. In those cases, CH and NH bond lengths were reset to 1.085 and 1.020 Å along the observed direction cosines of the atomic positions. The systems and a summary of the cell types and cell energies are shown in Table 1, the EFG and derived NQCC in Table 2, and the Mulliken populations for the atomic nuclei from the lattice calculations in Table 3. In the following discussion, we start with thioacetamide, which had been impracticable at the time of our earlier work [1, 2] owing to the low DZ exponents, and was a test case. We discuss the results individually, since the characteristics of each molecular system vary considerably.

Table 2. EFG (a. u.) and derived NQCC (MHz)[a] from the Lattice Calculations.

Thioacetamide					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N(1)(site1)	DZ	-0.5595			
N(1)(site2)	DZ	-0.5711	0.3955	0.1756	0.386
H(1)(site1)	DZ	+0.3469	-0.2053	-0.1417	0.183
H(2)(site1)	DZ	+0.3547	-0.2082	-0.1465	0.174
H(1)(site2)	DZ	+0.3450	-0.2048	-0.1401	0.188
H(2)(site2)	DZ	+0.3645	-0.2126	-0.1519	0.166
S(1)(site1)	DZ	+3.0725	-2.0701	-1.0025	
S(1)(site2)	DZ	+3.1056	-2.0835	-1.0221	0.342
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N(1)(1mol)	DZ(best)	-4.534(π)	2.773(R)	1.761(T)	0.223
N(1)(1mol)	DZ(scaled)	-3.383(π)	2.069(R)	1.314(T)	0.223
N(1)(site1)	DZ(best)	-2.642	1.874	0.768	0.419
N(1)(site1)	DZ(scaled)	-1.972	1.399	0.573	0.419
N(1)(site2)	DZ(best)	-2.655	1.868	0.829	0.386
N(1)(site2)	DZ(scaled)	-2.013	1.394	0.619	0.386
N(1)(site1)	Expt.[a]	1.922	1.399	0.523	0.456
N(1)(site2)	Expt.[a]	1.930	1.373	0.557	0.423
H(1)(site1)	DZ	+0.2331	-0.1380	-0.0952	0.183
H(2)(site1)	DZ	+0.2384	-0.1399	-0.0984	0.174
H(1)(site2)	DZ	+0.2318	-0.1376	-0.0941	0.188
H(2)(site2)	DZ	+0.2449	-0.1429	-0.1021	0.166
H(1)(site1)	Expt.[a]	0.2028	0.1146	0.0882	0.13
H(2)(site1)	Expt.[a]	0.1937	0.1143	0.0794	0.18
H(1)(site2)	Expt.[a]	0.1971	0.1104	0.0867	0.12
H(2)(site2)	Expt.[a]	0.1937	0.1114	0.0823	0.15
Imidazole					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N_1(H)	DZ(scaled)	-0.4798	0.4648	0.0149	0.938
N_3	DZ(scaled)	-0.7943	0.6055	0.1888	0.525
H_1(N)	DZ(best)	+0.2452	-0.1488	-0.0964	0.214
H_2(C)	DZ(lattice)	+0.3033	-0.1624	-0.1409	0.071
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N_1(H)	DZ(scaled)	-1.691	1.638	0.053	0.938
N_1(H)	DZ(cluster)	-1.828(π)	1.605(T)	0.223(R)	0.757
N_1(H)	NQR	-1.391	1.342	0.049	0.930
N_3	DZ(scaled)	-2.800	2.134	0.665	0.525
N_3	DZ(cluster)	-3.066(R)	1.942(T)	1.124(π)	0.267
N_3	NQR	-3.220	1.803	1.417	0.119
H_1(N)	DZ(lattice)	+0.1648	-0.1000	-0.0648	0.214
H_1(N)	DZ(cluster)	+0.1660	-0.0994	-0.0666	0.197
H_1(N)	NQR	0.1523	0.0902	0.0621	0.184
H_2(C)	DZ(lattice)	+0.2038	-0.1091	-0.0947	0.0708
H_2(C)	DZ(cluster)	+0.2266	-0.1201	-0.1066	0.0600
H_2(C)	NQR	0.1769	0.0945	0.0824	0.068
1H,4-Nitroimidazole					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N_1(H)	DZ(scaled)	0.4383	-0.4207	-0.0176	0.920
N_3	DZ(scaled)	-0.7815	0.6389	0.1426	0.635
N_4(O_2)	DZ(scaled)	0.5383	-0.4302	-0.1081	0.598
H_1(N)	DZ(best)	0.3433	-0.1957	-0.1476	0.140
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N_1(H)	DZ(scaled)	1.545	-1.483	-0.062	0.920
N_1(H)	NQR [18]	1.377	(-)1.230	(-)0.147	0.786
N_3	DZ(scaled)	-2.754	2.252	0.503	0.635
N_3	NQR [18]	(-)3.249	2.074	1.175	0.277
N_4(O_2)	DZ(scaled)	1.897	-1.516	-0.381	0.598
N_4(O_2)	NQR [25]	1.181	(-)0.863	(-)0.318	0.461
H_1(N)	DZ(scaled)	0.231	-0.131	-0.099	0.140
H_1(N)	NQR [25]	0.1609	0.0933	0.0676	0.160

Table 2 (cont).

Pyrazole					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N_1	DZ	0.5987(π)	-0.5806(R)	-0.0181(T)	0.940
$N_{1'}$	DZ	0.6473(π)	-0.6160(R)	-0.0313(T)	0.903
N_2	DZ	-0.9317	0.9243	0.0074	0.984
$N_{2'}$	DZ	-0.9462	0.8823	0.0638	0.865
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N_1	DZ	-2.827(π)	2.742(R)	0.085(T)	0.940
N_1	DZ/Trimer	-2.818(π)	2.744(R)	0.074(T)	0.947
N_1	NQR	(-)2.430(π)	2.167(R)	0.263(T)	0.784
N_2	DZ	-4.400	4.365	0.035	0.984
N_2	DZ/Trimer	-4.438	4.137	0.301	0.864
N_2	NQR	(-)3.769	3.387	0.382	0.798
1-Nitropyrazole					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N_1	DZ	-1.3149(π)	1.0700(R)	0.2450(T)	0.627
N_2	DZ	1.0916	-1.0416	-0.0500	0.908
N(NO_2)	DZ	-0.3054	0.2922	0.0132	0.913
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N_1	DZ	-4.634	3.771	0.863	0.627
N_2	DZ	3.847	-3.671	-0.176	0.908
N(NO_2)	DZ	-1.076	1.030	0.047	0.913
1-Acetylpyrazole					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N_1	DZ	-0.9067(π)	0.5885(T)	0.3181(R)	0.298
N_1	DZP/MP2	-0.5616(π)	-0.4490(T)	-0.1126(R)	0.599
N_2	DZ	1.1456(R)	-0.9738(T)	-0.1718(π)	0.700
N_2	DZP/MP2	0.8377(R)	-0.7818(T)	-0.0559(π)	0.866
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N_1	DZ	-3.1955(π)	2.0743(T)	1.1213(R)	0.298
N_1	DZP/MP2	-2.6524(π)	2.1205(T)	0.5319(R)	0.599
N_1	NQR	(-)2.9025(π)	2.2648(T)	0.6377(R)	0.5606
N_2	DZ	-4.0374(R)	3.4320(T)	0.6055(π)	0.700
N_2	DZP/MP2	-3.9561(R)	3.6920(T)	0.2642(π)	0.866
N_2	NQR	(-)4.4522(R)	3.7387(T)	0.7135(π)	0.6795
Pyrazine(I) and Tetramethylpyrazine(II)					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
I(N)	DZ	-1.151	0.762	0.389	0.325
II(N)	DZ	-1.188	0.781	0.407	0.314
I(H)	DZ	0.322	-0.170	-0.152	0.056
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
I(N)	DZ	-4.057(R)	2.686(π)	1.371(T)	0.325
I(N)	NQR	(-)4.857	3.730	1.127	0.536
II(N)	DZ	-4.187	2.752	1.436	0.314
II(N)	NQR	(-)4.672	3.389	1.283	0.451
1-Methylpyridinium Iodide					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ	-0.3260	0.2466	0.0795	0.513
H(Me)	DZ	0.3204	-0.1790	-0.1415	0.117
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N	DZ	-1.149	0.869	0.280	0.513
H(Me)	DZ	0.215	-0.120	-0.095	0.117
Pyridinium Chloride Hydrochloride					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ	0.2943	-0.2385	0.0558	0.612
H(N)	DZ	0.336	-0.1900	-0.1462	0.130
H(Cl)	DZ	0.3761	-0.1892	-0.1869	0.006
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N	DZ	1.037	-0.840	-0.197	0.612
H(N)	DZ	0.226	-0.128	-0.098	0.130
H(Cl)	DZ	0.253	-0.127	-0.126	0.006

Table 2 (cont).

Pyridine-N-oxide					
EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ	-0.1052(T)	0.0923(R)	0.0129(π)	0.755
NQCC	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
N	DZ	-0.371(T)	0.325(R)	0.045(π)	0.755
N	MW [49]	-0.858(T)	0.838(R)	0.020(π)	0.953
N	NQR [48]	+1.188(R)	-0.979(T)	-0.209(π)	0.648

[a] ^{14}N NQCC are scaled with the DZ scaling factor of 3.5244 MHz / a. u. unless otherwise stated. The best current value for Q_N is 20.2 mb, and is used for the MP2 calculations. Q_H used here is the recommended value 2.860 mb; [15]; 1 barn = 10^{-28}m^2 = 100 fm^2.

Table 3. Mulliken populations from the Lattice Calculations.

Pyrazole							
N_{1A}	N_{2A}	C_{3A}	C_{4A}	C_{5A}	H_{1A}	H_{3A}	
7.499	7.288	6.160	6.300	6.075	0.438	0.740	
H_{4A}	H_{5A}	N_{1B}	N_{2B}	C_{3B}	C_{4B}	C_{5B}	
0.762	0.738	7.524	7.259	6.195	6.302	6.071	
H_{1B}	H_{3B}	H_{4B}	H_{5B}				
0.430	0.732	0.746	0.736				
1-Nitropyrazole							
N_1	N_2	C_3	C_4	C_5	H_3		
7.256	7.144	6.088	6.361	5.912	0.706		
H_4	H_5	N_{NO_2}	O_1	O_2			
0.653	0.714	6.549	8.325	8.293			
1-Acetylpyrazole							
N_1	N_2	C_3	C_4	C_5	H_3		
7.356	7.106	6.165	6.307	5.980	0.767		
H_4	H_5	C_O	C_{Me}	H_{Me}			
0.785	0.723	5.436	6.641	0.775			
Imidazole							
	N_1	C_2	N_3	C_4	C_5		
Lattice	7.650	5.930	7.520	6.126	6.108		
Trimer	7.517	5.888	7.460	6.084	6.042		
	H_1	H_2	H_4	H_5			
Lattice	0.441	0.701	0.775	0.749			
Trimer	0.602	0.790	0.814	0.797			
4-Nitroimidazole							
N_1	C_2	N_3	C_4	C_5	H_1		
7.610	5.950	7.434	5.671	6.116	0.395		
H_2	H_5	N_{NO_2}	O_1	O_2			
0.653	0.642	6.736	8.390	8.402			
Pyrazine			Tetramethylpyrazine				
N	C	H	N	C_{ring}	C_{Me}	H	
7.235	6.165	0.717	7.273	5.805	6.736	0.774	
Pyridinium chloride hydrochloride							
N	C_α	C_β	C_γ	H_α	H_β		
7.442	6.109	6.210	6.071	0.691	0.734		
H_γ	H_N	H_{Cl}	Cl_1	Cl_2			
0.716	0.571	0.606	7.656	7.451			
1-Methylpyridinium Iodide							
N	C_α	C_β	C_γ	H_α			
7.278	6.038	6.242	6.126	0.700			
H_β	H_γ	C_1	H_{Me}	I			
0.711	0.714	6.494	0.755	7.739			
Pyridine-N-oxide							
O	N	C_α	C_β	C_γ	H_α	H_β	H_γ
8.633	7.047	6.157	6.187	6.112	0.655	0.749	0.715
Thioacetamide							
S_A	$C_{S,A}$	C_{Me}	N_A	$H_{N,A}$	$H_{N,A}$	$H_{Me,A}$	
16.405	5.672	6.404	7.744	0.638	0.633	0.835	
S_B	$C_{S,B}$	C_{Me}	N_B	$H_{N,B}$	$H_{N,B}$	$H_{Me,B}$	
16.420	5.662	6.416	7.743	0.629	0.631	0.832	

2.1. Thioacetamide

Thioacetamide shows 2 symmetry independent molecules in the unit cell [16, 17]: NQR double resonance from both sites have been observed in the NH_2 and ND_2 compounds with χ_{zz} 1.92MHz and η 0.45 (approx.) [18 -20]. The lattice calculation with a DZ basis set contains 72 atoms and 400 AO's per cell; the EFGs, after conversion to NQCC (Table 2) give very good agreement with the NQR experiment at the two ^{14}N sites, when the 'scaled' values are used; values with the 'best' value for Q_N (20.1mb) are rather larger than experiment. Single molecule calculations (Table 2) show the reduction in magnitudes is across all tensor elements, but especially the π-component. In our previous study of acetamide [21, 22], we calculated the EFG from the wave-function for a 4-molecule cluster, where one molecule was surrounded by its 3 nearest neighbours; the scaled EFG showed a change of NQCC from –4.061 MHz (η 0.074) for a single molecule to –2.899 MHz (η 0.439) for the cluster. The gross changes on condensation are in reasonable agreement with the NQR experiments, and the O and S system behave in a similar manner.

2.2. Azoles

Imidazole: An early part of our studies attempts to mimic the H-bonding effects on NQCC and involved trimer calculations on imidazole [23]. These successfully allowed assignment of the observed tensor elements. We now report lattice calculations using the same basis set, which enable a direct comparison of the trimer with the lattice. The space group ($P2_1/c$) shows 4-molecules to the unit cell, 232 AO's per cell; the results (Table 2) show that the agreement with experiment is improved at N_1H, but slightly poorer at N_3, although all results are acceptable. The tensor elements lie in similar directions in both series, as expected. The ^2H deuterium quadrupole coupling at H(N) is very close to experiment [24, 25] both in the cluster and lattice calculations, with the χ_{zz} lying along the HN bond. As with the cluster, the ^2H coupling at H(C) is in poorer agreement with experiment than that at N; although the present study gives better agreement with experiment(only a single set of data is known, with χ_{zz} 176.9 kHz, η 0.068), the present C_2H data are still high. It is not clear which centre relates to the observed ^2H coupling at H(C).

1H,4-nitroimidazole: NQR data have been reported [25], for a considerable group of substituted imidazoles; for many there are no crystallographic data, and for many others there is only weak perturbation of the ring system by the substituent(s). We consider one further case, where the ring is strongly perturbed, by a 4-nitro-group. The crystal structure [26] shows $P2_1/c$ with $Z = 4$ again. The DZ lattice calculation (CH and NH set to 1.085 and 1.02 Å) had 344 AO's per cell; the EFG and derived NQCC compared with the NQR data (Table 2) strongly indicate that χ_{zz} at N_3 is negative, consistent with a perturbed lone-pair, while (with less certainty) χ_{zz} at N_1 is positive and (differing from the parent heterocycle) lies in-plane and tangential to the HN bond axis. The (small) nitro-group experimental NQCC is never well reproduced by DZ basis sets, but the present results are indicative of χ_{zz} being positive. The ^2H NQCC at H_1(N), is calculated rather higher than usual, and this may result from the choice of the HN bond length 1.02 Å, with a (possible) change being provoked by the nitro-group.

Pyrazoles: We reported [27] a cluster calculation on the neutron diffraction structure of pyrazole previously. With two crystallographically independent molecules in the unit cell ($Pna2_1$) and hence $Z = 8$, this lattice [28] is beyond our own programme limit of 400 basis functions, but a parallel version of the code on a cluster of HP755 computers performed the 464 AO/cell calculation in 5.8 days. The NQR spectra [27] show closely spaced doublets for all lines, and the average values (Table 2) are compared with the EFG. Again the trimer calculation brings out all the important features of the lattice study.

1-Nitropyrazole: The most heavily perturbed pyrazole system for which there are both crystallographic and NQR data is the N-nitro-derivative [28]; a DZ basis calculation on this $P2_1/c$ system (344 AO's) gave high asymmetry parameters on all three N-atoms (Table 1). The tentative assignments [28] proposed the site of highest asymmetry (of the two sites identified) as N_1, but the present work suggests the reverse. If this conclusion is correct, then at N_1 χ_{zz} is the local π-direction, with π_{yy} as the radial direction from the ring; similarly, at N_2, χ_{zz} is positive, and tangential to the ring, and very slightly larger than the radial value, the classical lone-pair direction. This set of assignments, when compared with pyrazole itself, implies at both N_1 and N_2, a switch of the directions of the two in-plane axes at each centre. The high and low χ_π magnitudes at N_1 and N_2 are the same as in the parent compound.

1-Acetylpyrazole: Relative to pyrazole, the enhancement of the χ_{zz} values of 1-acetyl-pyrazole is similar to that of the 1-nitro-derivative; there is no crystal structure for the 1-acetyl-compound, but we have optimized the structure at the DZ/SCF level, to be consistent with the current work. There are two C_S symmetry conformers, with the CO group cis or trans to the N_2 atom. We find that the more stable conformer has the 1-CO and N_1N_2 bonds in a trans configuration; under these conditions, the values for χ_{zz} and (η) at N_1 and N_2 are −3.196 (0.298) and −4.037 MHz (0.700), respectively. The higher values of both χ_{zz} and η are on centre N_2 indicating that the provisional assignment for this compound is correct. This was confirmed by a DZP basis set calculation, with MP2 correlation, where the values (Table 2) are again very similar to experiment. The absence of an NH group reduces the intermolecular effects, by the absence of H-bonding, and single molecule calculations are likely to prove realistic.

2.3. Azines

Pyrazine and tetramethylpyrazine: Both these molecules crystallise in orthorhombic systems, with space groups Pmnn [30, 31] and Pbca [32] respectively; the NQR studies show that χ_{zz} (and η) are 4.857 (0.536) [33, 34] and 4.672 (0.451) [35] respectively. These are very similar compounds with comparable parameters, and the DZ basis set results (Table 1), which used a total of 136 and 496 AO's per cell, show how the basis AO's expand with only small molecular changes, when the number of molecules per cell number (Z) is large. The calculations do not distinguish between the small observed changes. A similar ordering of the tensor elements occurs; the principal difference between the calculated and observed NQCC for both compounds is the balance between the lone-pair terms (χ_{zz}) and the π-values (χ_{yy}); we observed a similar effect with the azoles [27].

2.4. Protonated and other charged Pyridine rings

The NQR spectra of a number of pyridines, their salts and quaternary compounds have been reported [36 - 41]. Many of the principal values of χ_{zz} are very similar to eachother, and asymmetry parameters are also similar; there is a poor overlap with diffraction structures of the solids. For pyridine, both anhydrous and trihydrate structures have been reported; for the space groups in question, the number of atoms per cell (44 for the anhydrous form) or AO's per cell (trihydrate) are too large for current dimensions of **CRYSTAL-92**. We chose to study one case of the the protonated pyridine ring, and a single quaternary compound. The NQR data for (pyridine·H)$^+$ X$^-$, where X is HSO_4,NO_3, Cl, Br, etc. show a trend of reduction in χ_{zz} across that sequence, with high η in all cases.

Pyridinium dihydrochloride: There are problems with the selection of a pyridinium ion, since disorder of the $C_5H_5NH^+$ group with respect to the anion occurs in several obvious choices. The simplest compounds for which x-ray data are available are the chloride [42] and nitrate [43], but both have poorly defined atomic positions, and the former has $Z = 8$, making the lattice calculation impracticable. We chose pyridinium chloride hydrochloride [44], where the crystal shows H$^+$ coordinated to the N-atom, and the other H atom associated with 2CL(-), but with two very different H-Cl bonds. The geometry around the ring of the mono- and di-hydrochloride species is very similar. The CH/NH bonds (not found) were reset as above.

The DZ basis and the Hay and Wadt ECP for the chloride ion leads to 30 atoms per cell with only 164 AO's. The principal EFG (q_{zz}) is positive at ^{14}N with a derived NQCC of +1.037MHz, and asymmetry of 0.612; these values are typical of those found for the protonated pyridine ring, but indicate that χ_{zz} is positive for these salts.

N-methylpyridinium iodide: This orthorhombic system [45] has space group $P2_12_12_1$ and has been studied by NQR as the trideutero-compound [38]. In contrast to the cation above, the principal value for χ_{zz} is negative, and the high asymmetry parameter is unexpected in the light of the three C atom neighbours and the reported NQR data. However, the NQR data are based upon the assumption that the two lines observed are in fact ν_+ and ν_-, since ν_0 was not found. The principal axis is perpendicular to the local NC_3 plane.

Pyridine-1-oxide: An x-ray study of this compound shows [46] 2 crystallographically independent molecules in the orthorhombic $C222_1$ space group. H-atoms were inserted as previously, using the equilibrium structure of the molecule to position the H atoms, in the absence of crystallographic data. These data are very similar to the complete microwave structure [47]. The ^{14}N NQR data [38, 48] and microwave ^{14}N data have been reported [49]. A previous Townes-Dailey analysis [48] for ^{14}N gave the principal axis χ_{zz} lying along the NO-bond axis, with the out-of-plane term as χ_{xx}. The asymmetry parameter is high (0.648), and χ_{zz} is low (1.188MHz). This is in considerable disagreement with the microwave data, however; since the axes in such MW experiments are well-defined, the a-axis term (+0.838 MHz) is χ_{yy} lying along the NO-bond axis, while the largest value is χ_{bb}, with the identities $x = c$, $y = a$, $z = b$, and η 0.953. The present lattice calculation shows the two different ^{14}N sites, but does not give good values for the tensor elements. The closeness of the tangential(T) and radial terms(R) makes it impossible to be sure that the MW order is retained in the solid.

2.5. Mulliken Populations

One difference between the lattice and cluster calculations (Table 3) lies in the Mulliken analyses at all centres in which imidazole is typical; in both series, N_1 is more negative than N_3, but the N_1H bond is more polar in the lattice, and this is true of the CH polarity as well. In part this must be a result of small contributions to the atomic populations arising from the overlap populations with more distant centres in the lattice, which have no counterpart in the molecular calculations. In the previous cluster calculations, the central molecule was not strictly neutral with respect to its neighbours, whereas exact neutrality is present in the lattice calculations.

Although Mulliken populations are dependent upon the basis set, only rarely does this affect the

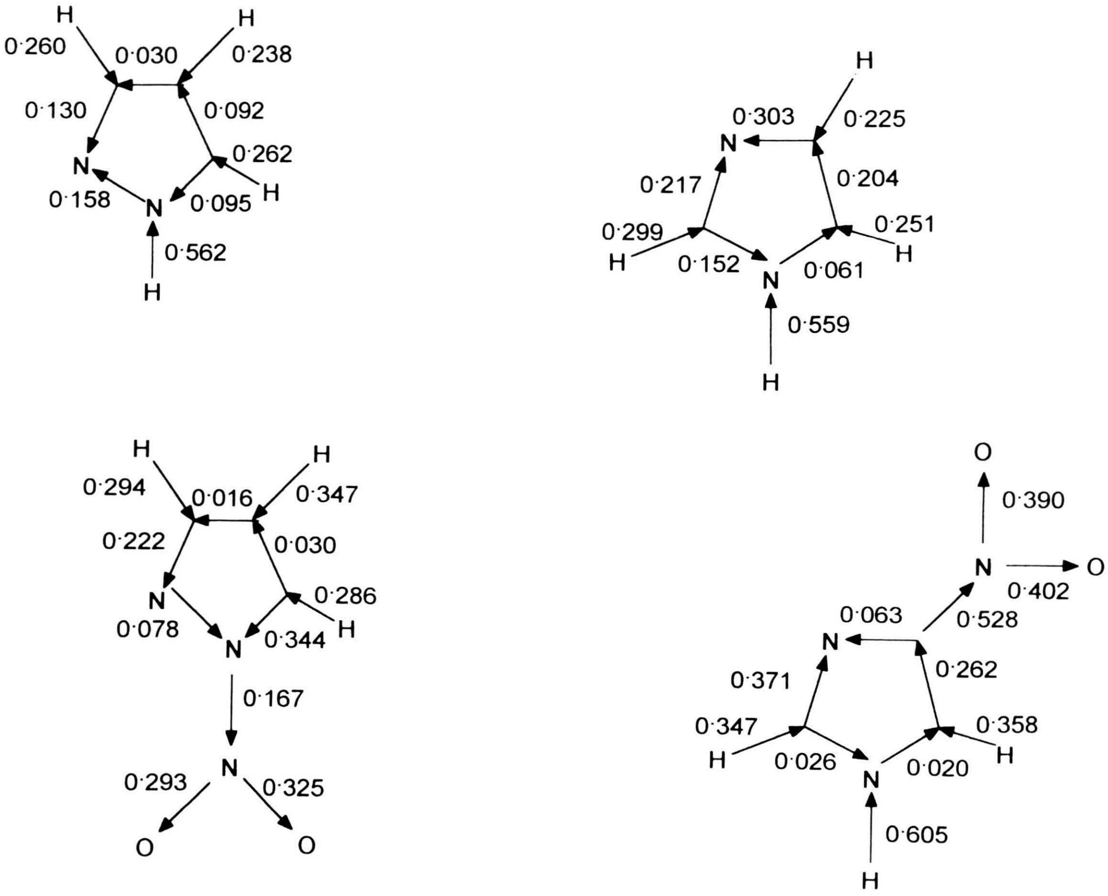

Fig. 1. Total bond population moments (local bond populations based on Mulliken analyses; arrowheads are the negative end of the local dipole).

direction of the dipole moment, when DZ or larger bases are used. The very steady characteristics within a series of molecules with a fixed basis set are long known. In the following discussion, we make use of the long-established concept of bond dipoles. Dissection of the Mulliken charges by solution of a set of linear equations [50] enables the population to be assigned to local contributions, as shown in Figure 1. The H-atoms are effectively electron donors to all attached atoms, such that NH and CH bonds provide most of the polarity in the non-oxygenated compounds. For imidazole, the CH bond populations differ quite strongly at the 5,4 and 2-positions, while pyrazole has smaller differences. Although more extensive basis sets will reduce all the bond polarisation, from previous experience we can expect the relative effects to remain.

Comparison of imidazole with pyrazole (Fig. 1) shows that the overall charge separations have dipoles directed from the α-positions towards the β-positions in imidazole (positive to negative respectively, in this discussion). The position with pyrazole is more complex, but the common feature is drift of electrons from C to N. It is of interest to compare the parent heterocycle with the nitro-derivatives (Table 3). The bond dipoles in Fig. 1 show the principal effects; the first main point is that the bond dipoles in azole and nitroazole all lie in the same direction at comparable positions (although the magnitudes differ considerably), except at the point of attachment. This consistency is surprising and suggests that the bond dipole directions are a feature of the particular ring system, since the nitro-group is one of the strongest perturbing groups. In the pyrazoles, the 1-nitro-compound removes about 0.2e from the ring, most of this from the CH bonds, and particularly the 4-CH bond. The CN bond dipoles are significantly larger in the nitropyrazole. The attachment of the NO_2 group to an N atom, rather than C in the imidazole, limits the pull of the O-atoms in the former. The pair of imidazoles behaves similarly, but here the polarisation of the C_2N_3 and C_5C_4 bonds is much increased in the nitro case.

The pair of pyridinium cations, 1-methylpyridinium iodide and pyridinium chloride hydrochloride, have anions (I and HCl_2) with similar net charges of 0.74 e and 0.71 e, respectively. This is the total charge transfer from ring to halide. The ring CH bond dipoles are effectively identical at similar positions, and the CC ring polarisations have increasing polarity, $C_\gamma C_\beta$ 0.08, $C_\beta C_\alpha$ 0.14, and $C_\alpha N$ 0.38 e respectively. The higher net charge on the N atom in the protonated form is a direct result of the H atom being a better donor (0.57 e) than the CH_3 group (0.24 e).

Pyridine-N-oxide, is normally drawn as N^+-O^-, but other canonical forms involving N^+=O with C_α^- or (better) C_γ^-, are used to explain the ready electrophilic substitution at C_γ on the basis of ground state electron distribution. The dipole moment strongly implies dominance of the first form. Indeed the present CH bond dipoles are very similar to the pyridinium salts, and the progressive polarisation of the CC and CN ring polarisations, which have increasing polarity, $C_\gamma C_\beta$ 0.09, $C_\beta C_\alpha$ 0.15, and $C_\alpha N$ 0.35 e, respectively, is strongly reminiscent of the pyridinium ions. The net charge transfer from ring to O is about 0.63 e, rather than 1.0 e from the classical form.

2.6. Conclusions

An important finding of the present work is that the trimer and tetramer cluster studies reported previously for the imidazole and pyrazole do give results very similar to the full lattice, with the same basis set. Hence we can feel confident that the related cluster calculations are likely to be correct. The new study, on single molecules for 1-acetylpyrazole reverses the assignment to that previously published, and the present seems more plausible. The agreement with NQR data for these simple imidazoles and pyrazoles is satisfactory. Although larger basis sets are likely to improve agreement of a particular tensor element with the assigned NQCC, the results are unlikely to reverse EFG to NQCC assignments, except in a few cases where the asymmetry is very high. These latter cases, by making two EFG/NQCC pairs close in magnitude, but reversed in sign, are clearly the most problematic.

A detailed analysis of the charge distributions in several of the compounds shows the high extent of bond polarisation; when this is dissected into local bond dipoles, strong similarities between related compounds occur.

The azine calculations show a phenomenon which is now appearing general; there are few cases where NQR data *and* neutron *or* x-ray diffraction structures are known. At the time of writing there were 228 pyridine structures in the Cambridge Crystallographic Database, and almost none of these have NQR data; the converse is true with NQR studies on some 30 compounds. Hence there is an urgent need for new data on critical members of these and other simple ring systems by *both* techniques.

A further problem is the size of many lattice structures in terms of atoms *and/or* atomic orbitals per cell, a feature which is critically dependent upon the space group, especially the orthorhombic types. The direct SCF method, although extremely expensive in CPU-time, does allow a solution to large calculations, but programme limitations can be unexpectedly exceeded, even by simple cases such as pyridine.

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