Quadrupole Coupling in some H-bonded Organic Systems by *ab initio* Lattice Calculations of Electric Field Gradients *

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We present *ab initio* Hartree-Fock lattice calculations performed in the unit cell environment, to compute a wave-function and the derived electric field gradients for the bulk material. These calculations differ from cluster calculations by including the effects of more distant neighbour molecules. Examples considered are ammonia, formamide, oxamide, urea, thiourea, uracil, parabanic acid, alloxan, guanidine bicarbonate and melamine.

1. Introduction

Our previous studies of a variety of organic and inorganic molecules, each containing one or more ^{14}N, $^{10,11}B$ or ^{32}S as quadrupolar nuclei, came into two classes; (a) studies of individual molecules at equilibrium [1–3] and (b) small groups of molecules [4–6], where a test molecule was surrounded by its nearest shell of neighbours from the crystal lattice. In (a) comparison was with gas-phase data (usually microwave spectral results); the results of (b) were compared with NQR data from the solid state. The present paper will present a number of results using 'CRYSTAL-92', an *ab initio* Hartree-Fock SCF programme for periodic systems [7]; this programme computes the electronic wave-function in the reciprocal space of the unit cell system and hence generates a wave-function which represents the bulk material, rather than just a local environment. More detail concerning the methods is given in our recent paper on inorganic molecules [8], and in the papers by Saunders et al. [7, 9, 10].

2. General Methods

This paper contains results obtained by two methods: (a) conventional SCF studies with a cluster(Cn) of molecules, at their crystallographic positions. These calculations used the GAMESS-UK program, as in our previous work [1–6]. Lattice calculations were performed with CRYSTAL-92 as described below. The data input to CRYSTAL-92 is the crystallographic space group, unit cell parameters, the asymmetric unit, and the basis set. The basis functions are Bloch functions of GTO type. The principal problem restricting the choice of a basis is the storage of 2-electron integrals during the calculation. Since CRYSTAL-92 computes electron repulsion integrals over products of radial functions and products of spherical harmonics, there is considerable saving of CPU-time and 2-electron integral filespace by the use of shared sp-radial functions, as in the Pople STO-NG and N-31G series. We made use of these functions in each series of calculations, with 4-31G (H atom) [11] 6-21G and 6-31G [12, 13] for C-F, and 66-21G for Na–Cl [14]. Since shared exponents for sp-GTOs are generally an approximation, other bases were used where the number of atoms in the unit cell permitted. Thus, we used a double (DZ) or triple zeta basis with polarisation (TZVP) for some small system calculations [15–17]. These are comparable with our previous work [4–6], and generally give reliable values for the NQCC when compared with NQR data. Similarly, the Roos and Siegbahn [18] 10s6p sets and Huzinaga [19] 14s10p for S contracted to DZ, give better flexibility than 66-21G sets, and were used where practicable.

The electric field gradients (q_{ii}) were converted to the nuclear quadrupole coupling constants (NQCC) by means of the equation

$$\chi_{ii} = e^2 Q_Z q_{ii}/h = 234.96\, Q_Z\, q_{ii}, \qquad (1)$$

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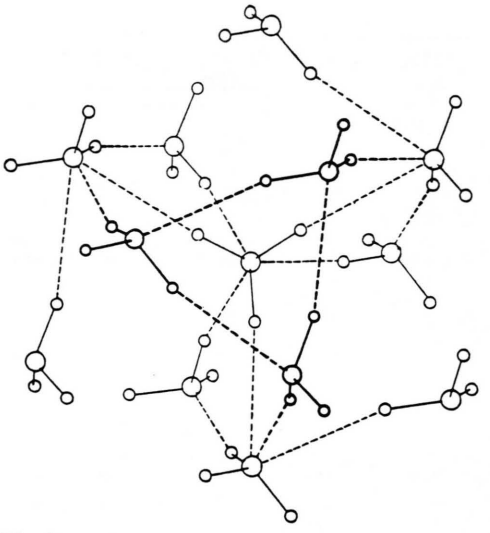

Fig. 1

where the term 234.96 also contains the conversion between the various units. In our previous work, we treated the value of Q_Z (usually described in mbarn ($=10^{-31}$ m^2) units) as a scaling parameter, using a correlation of EFG (q_{ii}) against χ_{ii}, to evaluate the appropriate Q_Z [1–3].

Thus the scaled DZ and TZVP correlation constants were 3.5244 and 4.0111 MHz/a. u. (15.000 and 17.071 mbarn), respectively; these are here used for the ^{14}N studies as the 'scaled' NQCC; however, the main results used the best current value for Q_N (20.2 mb [20]). In (1) the signs of the EFG elements have been reversed relative to our previous work, since the internal definition of the EFG in the GAMESS-UK program is such that a negative sign is appended.

3. Results

3.1 The Ammonia Crystal

Prior to the study with CRYSTAL-92, we performed calculations on groups of 1, 4, 7, 10, and 13 molecules at the crystallographic orientation [21, 22] as shown in Figure 1; this approach has been employed previously with some success with a DZP basis [23]. An equilibrium structure for the heptamer, albeit with a very small basis set, has also been obtained [24]. The results for the small clusters show the decrease in χ_{zz} as the groups of three neighbours are added, but the values are always high relative to the NQR data

Table 1. The ammonia system: Energies and ^{14}N EFG.

(a) DZ and DZP clusters at the neutron diffraction structure, SCF and CI results.

Cluster size	Basis	Method	Energy a.u.	^{14}N NQCC χ_{zz}/MHz	Scaled NQCC χ_{zz}/MHz
1	16	DZ/SCF	−56.16813	−5.7505	−4.2704
4	64	DZ/SCF	−224.68106	−5.1463	−3.8218
7	112	DZ/SCF	−393.21169	−4.6536	−3.4559
10	160	DZ/SCF	−561.73602	−4.6883	−3.4816
13	208	DZ/SCF	−730.24559	−4.7438	−3.5229
13	208	DZ/CI	−730.50968 @	−4.7329	−3.5148
1	31	DZP/SCF	−56.20093	−5.3437	
4	79	DZP/SCF	−224.71309	−4.7975	
7	127	DZP/SCF	−393.24189	−4.3807	
10	175	DZP/SCF	−561.76615	−4.4101	
1	31	DZP/CI	−56.39087	−4.8923	
4	79	DZP/CI	−225.19907	−4.4946	
7	127	DZP/CI	−393.98794	−4.1893	
10	175	DZP/CI	−561.96421	−4.2815	

(b) Cell studies

Cell N Basis	Basis type	Cell energy a.u.	^{14}N EFG q_{zz}/a.u.	NQCC χ_{zz}/MHz	Scaled NQCC χ_{zz}/MHz
64	DZ	−224.70791	−0.9950	−4.7223	−3.5069
116	6-21G*/3-21G*	−224.63819	−1.0238	−4.8592	
116	6-31G*/4-31G*	−224.09253	−0.9758	−4.6311	
120	DZP	−224.83044	−0.9354	−4.4398	

(Table 1). CI has only a marginal effect. The CRYSTAL-92 cell calculations produce almost identical results for the DZ and DZP bases as the 10/13 molecule clusters. This is a satisfactory result justifying our approach of studying single shells of neighbours around the test site [4–6] and the use of scaled valus for Q_N to bring the NQCC close to experimental values.

3.2 The Formamide and Oxamide Crystals

Our previous formamide study [25] used calculations of up to 6 molecules, such that all nearest neighbours were included [26, 27]. In the present work, several basis sets were used, and the comparison is with the DZ results from the two studies (Table 2). The scaled values for the ^{14}N NQCC (footnote to Table 2), provide the link to [25]. The asymmetry parameter falls towards the experimental NQR value of 0.378 [28] as the basis increases, while the NQCC is best reproduced by the 6-21G** and DZ basis set results. Again there is a considerable similarity between the 6-molecule DZ calculation and the corresponding lattice calculation.

Table 2. The formamide crystal.

Cell N Basis	Basis type	Cell energy a.u.	^{14}N χ_{zz}/MHz	^{14}N η	^{17}O χ_{zz}/MHz	^{17}O η
132	5s1s1s/2p1p	−673.97398	−2.0830	0.7385	7.0543	0.8907
132	6-31G	−675.11328	−2.1889	0.7685	8.0964	0.8801
228	6-21G**	−674.86583	−2.0508	0.4705	6.4935	0.8932
144	DZ[a]	−675.39373	−3.5642[b]	0.5010	10.1147	0.6524
216	DZ 6 mols	−1013.3052	−2.7565	0.4737		

[a] The DZ atomic populations at the various centres are: O [8.644], N [7.631], C [5.749], H(1) [0.612], H(2) [0.612], H(3) [0.761] (CH).
[b] Scaled ^{14}N NQCC for the 2 DZ rows (144 and 216 basis) are: −2.6470, −2.7566 MHz, respectively.

Table 3. The oxamide crystal energy (a.u.), EFG (a.u.), and NQCC (MHz)[a, b].

Cell	Basis	Cell energy	q_{zz}	χ_{zz}	η
62	6-31G	−336.02353	−0.4908	−2.3292	0.6131
68	DZ[a]	−336.53325	−0.7201	−3.4179[c]	0.4939

[a] The correct coordinate for H(2) is $z = 0.0896$ [34].
[b] The DZ atomic populations at the various centres are: O [8.611], N [7.847], C [5.501], H(1) [0.532], H(2) [0.509], the 6-31G results are similar.
[c] The scaled NQCC for the DZ basis result is −2.5382 MHz.

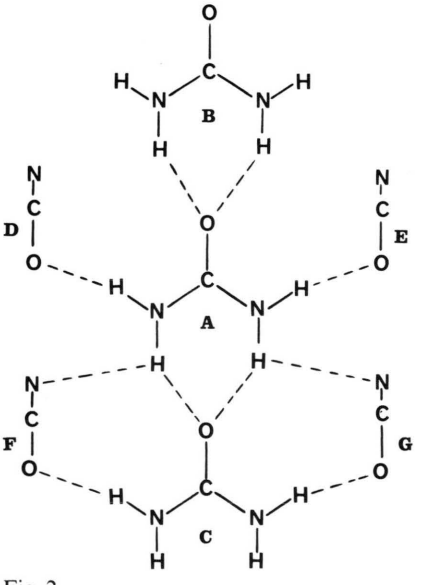

Fig. 2

The oxamide crystal [29] shows quadrupole coupling almost identical to that of formamide above, with the two basis sets used here. This is unexpected, since the replacement of H(C) in formamide by H_2N–CO as in oxamide introduces a considerable perturbation in the atomic populations; the corresponding DZ populations are shown in the footnotes to Table 3. Thus, although the site is quite remote from the change, the negligible effect must arise from a balance of factors, in which the different H-bonding must play a part. The N atom in oxamide seems to be much more negative than in formamide, but this is achieved by σ-donation from each of its neighbours, 2 H and C atoms. The result is a balanced effect at N, with no resultant change in χ_{zz}.

3.3 The Urea Crystal

Urea has planar molecules and, unusually, 4 H-bonds to each O [30, 31]. The electron density has been discussed in relation to both the crystal structure [33] and electronic structure calculations of the isolated molecule [34]. The electronic structure has also been studied by a lattice calculation of the present type, but the primary interest was in the difference density relative to the monomer; no EFG's were reported [34]. In the gas phase, the NQCC have been identified [35, 36]; the C_2 symmetry axis of the C_{2v} molecule is along the *b*-axis, with χ_{cc} −4.053, the out-of-plane value being χ_{zz}, and η 0.0683. Since only the inertial axis values have been obtained, the position of the in-plane axes remains to be determined; the present study finds the χ_{yy} element to lie 5.42° from the CN bond and angled towards the O atom with the DZ basis. This angle is increased to 12.55° with the DZP basis, but on general principles we suspect the former is the more reliable value. The NQR of urea is complex [37, 38]; the NQR parameters [37] are χ_{zz} (−)3.507 MHz with η 0.323, where the sign is assumed and the asymmetry parameter is quite different from the isolated molecule.

In the cluster study, 7 molecules (Fig. 2) were chosen such that one member (A) was fully enclosed by

Table 4. Urea ^{14}N EFG and derived NQCC.

N Basis	Type	q_E	q_I	q_π	η
(a) Single molecule equilibrium (equil) and neutron diffraction (neut) structure[a].					
48	DZ (equil)	+0.5198	+0.7408	−1.2607	0.1753
80	DZP (equil)	+0.5395	+0.6498	−1.1893	0.0927
48	DZ (neut)	+0.5326	+0.7119	−1.2445	0.1441
80	DZP (neut)	+0.5448	+0.6248	−1.1696	0.0684
76	6-21G**(neut)	+0.5053	+0.5640	−1.0693	0.0549
44	6-31G (neut)	+0.5246	+0.6300	−1.1546	0.0913
(b) Lattice (L) and *n*-clusters (Cn) at neutron diffraction structure.					
88	6-31G L	+0.3033	+0.6135	−0.9168	0.3384
96	DZ L	+0.3030	+0.7090	−1.0120	0.4012
160	DZP L	+0.3353	+0.6216	−0.9569	0.2991
152	6-31G** L	+0.3302	+0.5519	−0.8821	0.2513
192	DZ+MB C7	+0.3376	+0.7169	−1.0544	0.3597

N Basis	Type	χ_E	χ_I	χ_π
(c) DZ scaled comparisons with experimental data[b,c]				
48	DZ C1	+ 1.8771	+ 2.5090	− 4.3861
192	DZ+MB C7	+ 1.1898	+ 2.5267	− 3.7165
96	DZ L	+ 1.0679	+ 2.4987	− 3.5666
	NQR	(+)1.1871	(+)2.3199	(−)3.5070
	MWAVE	+ 1.888	+ 2.165	− 4.053

[a] In C_{2v}, χ_π is the same as χ_{cc}, and is out-of-plane of the molecule. I lies 5.419° (DZ basis) from the CN bond and towards the O atom; this is close to the Internal bisector of the HNH angle. E lies close to the External bisector of the HNH angle (and is 90° from I).

[b] The Mulliken analyses for the urea molecule vary by only about 5% over a basis set change from 42 to 192 AOs. The values for the DZ basis at O, N, C, H (outer), H (inner) are: 8.733, 7.898, 5.340, 0.526, 0.539 e, respectively.

[c] Urea total energies (a.u.) are: DZ+MB (C) −1563.79319, DZ (L) −447.82456, 6-31G (L) −447.84595, DZP (L) −448.03224, 6-31G** (L) −448.04697.

nearest neighbours (B–G); because of SCF limitations in atomic orbital size (AOs), the basis was DZ at the central molecules (A–C), and minimal basis (MB) elsewhere. The tensor χ_{yy} lies 5.28° from the CN bond, but on the opposite side to the free molecule. Thus the direction of χ_{yy} has shifted by 10.70°; the tensor elements are little changed. The assumption of the Townes-Dailey theory that the tensor elements lie along one of the molecular bonds, are clearly only approximately true. Hence, atomic populations based upon such analyses are also suspect.

The CRYSTAL-92 study used up to 160 AOs (DZP basis) per cell of 16 atoms. All of the results are shown in Table 4. The agreement between both the microwave data for the isolated molecule, and the numerical agreement between the NQR tensor elements and the cluster or lattice calculations is so good that the assignment of tensor directions is unambiguous.

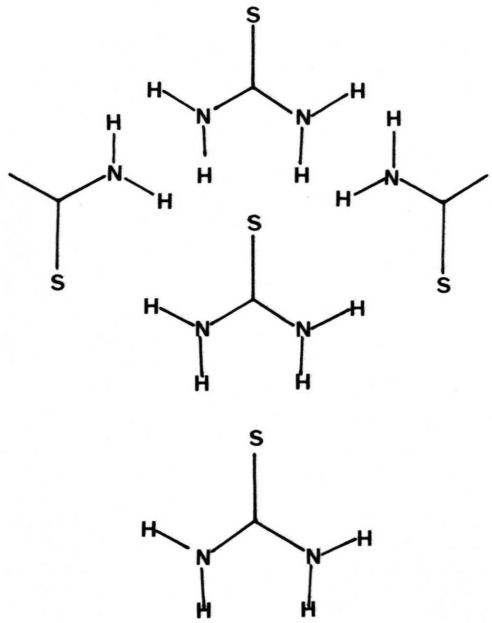

Fig. 3

3.4 The Thiourea Crystals

At 293 K, thiourea has space group Pnma [39] (Fig. 3), but at low temperatures, the ferroelectric phase [40, 41] is $Pmc2_1$ (now $P2_1ma$) [40]. The ferroelectric effect arises from tilting of molecules such that the resultant dipole moment is non-zero, leading to two sites where the molecules make angles of 19.6 and 29.5° to the *b*-axis. The room temperature form has the (C_{2v}) molecules lying at an averaged angle of 26.6° to the *b*-axis. Various analyses have been made on the neutron and X-ray analyses [42–44] to determine experimental electron density distributions. The NQR spectrum of the low temperature phase shows the two nonequivalent sites [45], but with very similar parameters. The NQR spectrum disappears as the temperature is raised towards ambient values.

The cluster calculations (Table 5) for both modifications show the difficulties of such studies, where a problem is the choice of the unit, so as to avoid edge effects. Further, it was difficult to obtain SCF convergence for the chosen clusters, and the numerical results are not completely consistent in energy. The EFG results show similar form but variable η. The low temperature form results from the 175 basis set 5-molecule clusters (one for each site) and the lattice calculation which obtains both sites in the one cal-

Table 5. The thiourea system.

(a) Nuclear quadrupole coupling parameters[a, b, c] *at equilibrium.*

N Basis	Type	χ_E	χ_I	χ_π	η	α
56	DZ C1	−0.5633	−0.7154	+1.1534	0.2406	+10.34
92	DZP C1	−0.4562	−0.6445	+1.1007	0.1711	+15.63

(b) Thiourea Pnma 273 deg structure.

N Basis	Type	q_E	q_I	q_π	η
196	SV+DL	+0.3324	+0.5934	−0.9257	0.2820
199	DZ+MB C5	+0.2938	+0.7202	−1.0140	0.4205
212	6-31G L	+0.2837	+0.5885	−0.8722	0.3494
224	DZ L[d]	+0.2856	+0.6823	−0.9679	0.4098
320	6-31G** L	+0.2961	+0.5336	−0.8296	0.2861

(c) Thiourea Pmc2$_1$ (P2$_1$ma) low-temperature structure.

N Basis	Type	Energy/a.u.	q_E	q_I	q_π	η
175	DZ C5 (site 1)	−2728.12489	+0.2499	+0.7158	−0.9658	0.482
175	DZ C5 (site 2)	−2728.04639	+0.2429	+0.7850	−1.0279	0.527
231	DZ+C7 (site 1)	−3818.79834	+0.0701	+0.5883	−0.9694	0.784
231	DZ+C7 (site 2)	−3818.81419	+0.1678	+0.6140	−0.7818	0.571
212	6-31G L	−2029.72743				
	site 1		+0.2621	+0.5908	−0.8529	0.385
	site 2		+0.2561	+0.5837	−0.8397	0.390
224	DZ L	−2186.24476				
	site 1		+0.2718	+0.6896	−0.9615	0.435
	site 2		+0.2650	+0.6808	−0.9459	0.440

(d) Thiourea comparison of calculated and experimental NQCC.

N Basis	Type	χ_T	χ_R	χ_π	η
231	DZ C7 (site 1)	0.2506	2.0734	−2.3240	0.784
231	DZ C7 (site 2)	0.5914	2.1640	−2.7554	0.571
175	DZ C5 (site 1)	0.8808	2.5228	−3.4039	0.482
175	DZ C5 (site 2)	0.8561	2.7667	−3.6228	0.527
212	6-31G (site 1)	1.2438	2.8041	−4.0479	0.385
212	6-31 G (site 2)	1.2154	2.7701	−3.9855	0.390
nqr 77 K	site 1	0.9437	2.1779	−3.1216	0.3954
nqr 77 K	site 2	0.9407	2.1589	−3.0996	0.3930

[a] The equilibrium geometry inertial axis data are χ_{aa} 1.9852, χ_{bb} 2.0797 MHz (dipole moment along *a*-axis).

[b] The direction given by α is the angle ZNC, the position of positive Z being chosen to have a dihedral angle SCNZ of zero.

[c] In C_{2v}, χ_π is the same as χ_{cc}, and is out-of plane of the molecule. I lies close to the in-plane Internal bisector of the HNH angle, and lies along ZN. E lies close to the external bisector of the HNH angle, and lies along ZN. E lies close to the external bisector of the HNH angle (and is 90° from I).

[d] Thiourea Mulliken populations (DZ basis) at S, C, N, H (inner), H (outer) are (Pnma) 16.473, 5.539, 7.775, 0.612, 0.607, the values for the Pmc2$_1$ structure are nearly identical.

culation, are reasonably consistent. The 231 basis set 7-molecule cluster with an additional 2 molecules, which were the start of another shell of neighbours, is incomplete. The effect on the EFG is quite dramatic and clearly unbalances the calculation. All of these calculations confirm that the direction of χ_{zz} lies out of the local plane, and the in-plane values are significantly distorted from the CN bond axis. In the free molecule, the DZ basis set results show the χ_{yy} tensor element lying 10.34° from the CN bond, and towards the S atom, i.e. a similar effect to that in urea. The cluster calculations suggest that the tensor element is little changed in position in the crystal.

3.5 The Uracil, Parabanic Acid and Alloxan Crystals

The NQR of uracil has been obtained by several groups of workers [46–49]; two groups have obtained data for the N1 and N3 sites in the crystal [46, 47]. There are no recent X-ray or neutron diffraction studies of this molecule, and the early ones [50, 51] do not give realistic NH or CH bond lengths; the structure is shown in Figure 4. The CH and NH bonds were set to 1.080 and 1.020 Å, respectively. The tensor elements (Table 6) at N1 and N3 which lie close to the NH bonds (χ_R with the smallest values), have only about 1.5° from the NH axis to χ_R. At both centres N1 and

Table 6. Results for uracil, parabanic acid, alloxan and guanidine bicarbonate.

(a) Calculated electric field gradients 6-31G basis.

Molecule	N Basis	Centre	q_R	q_T	q_π	η
Uracil	320	N(1)	+0.1163	+0.5460	−0.6623	0.649
		N(3)	+0.1135	+0.5427	−0.6562	0.654
Parabanic A	304	N	+0.2626	+0.5711	−0.8337	0.370
Alloxan	376	N	+0.5683	+0.2215	−0.7898	0.439
Guanidine HCO_3	344	N	+0.2483	+0.6712	−0.9196	0.460

(b) Comparison of calculated and experimental NQCC.

Molecule	N Basis	Site	χ_T	χ_R	χ_π	η
Uracil	320	N1	+ 0.5520	+ 2.5915	− 3.1435	0.649
		N3	+ 0.5386	+ 2.5758	− 3.1144	0.654
	NQR	N1	(+)0.613	(+)2.014	(−)2.627	0.533
		N3	(+)0.596	(+)1.986	(−)2.583	0.538
Guanidine HCO_3	344	N1	+ 3.1861	+ 1.1786	− 4.3646	0.460
Guanidine Acetate	NQR	N1	(+)2.4142	(+)0.7265	(−)3.1407	0.5374
Guanidine Carbonate	NQR	N1	(+)2.5120	(+)0.8498	(−)3.3618	0.4944

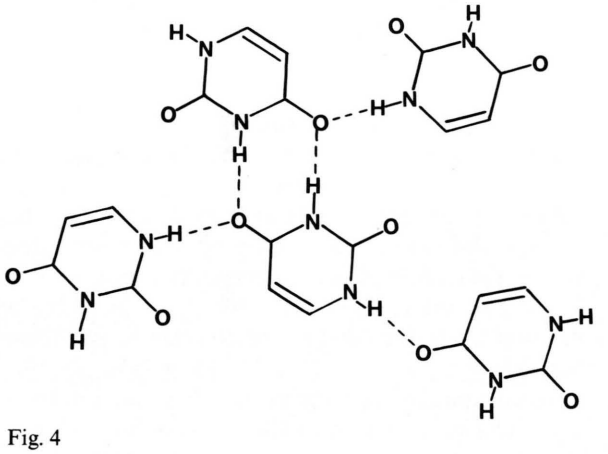

Fig. 4

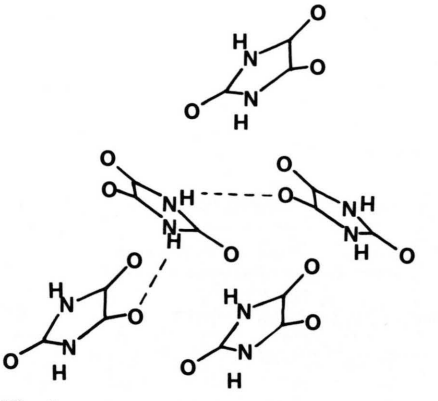

Fig. 5

N3 the principal value χ_{zz} lies out-of-plane, with that at N3 marginally larger in the calculation, but reversed in the NQR assignment [52]. The closeness of χ_{zz} to the NH bond is a characteristic of the neighbours being both C atoms, even though the attached atoms to these are quite dissimilar.

The parabanic acid structure is shown in Figure 5 [52]. The differences in the X-ray structural parameters are sufficiently large for treating the molecule as C_S symmetry rather than the expected C_{2V}, which it shows in solution. Few details of the NQR study are available [53]. The present work shows this is a typical amide-like molecule; like uracil, the principal value of the EFG q_{zz} lies out of the local plane; however, the smallest tensor element lies about 4.2° to the NH bonds and towards the 4-CO group.

Alloxan (Fig. 6) [54], is closely related to parabanic acid, with a further CO group; the NQR data of this important biologically active species are apparently not published. The EFG tensor elements lie in similar directions to those of parabanic acid; again the tensor element χ_{xx} lies along the NH bond.

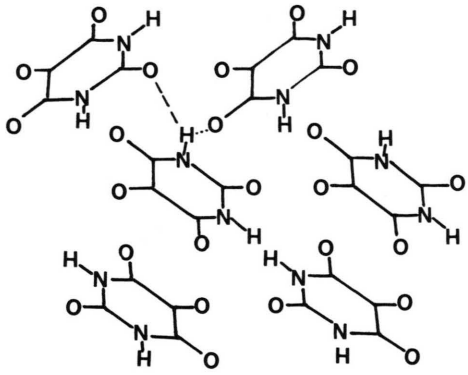

Fig. 6

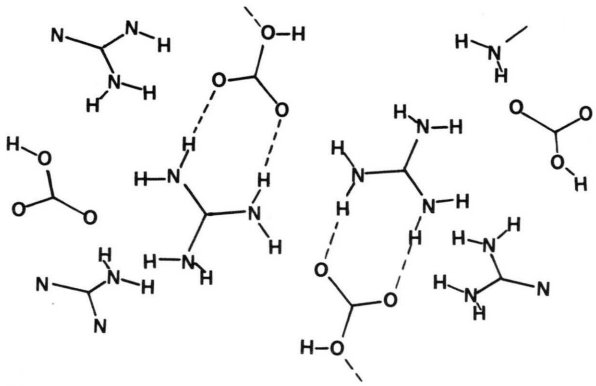

Fig. 7

Table 7. Total energies (a.u.) and Mulliken populations.

Molecule	Total energy	Mulliken populations			
Molecule		N1	C2	N3	C4
Uracil	−1648.87362	7.851	5.010	7.916	5.153
		C5	C6	O2	O4
		6.488	5.690	8.627	8.751
		H1	H3	H5	H6
		0.701	0.663	0.593	0.556
Molecule		N1	C2	N3	C4
Parabanic A		7.860	4.920	8.596	7.868
		C5	O2	O4	O5
		5.182	8.596	8.583	8.620
		H1	H3		
		0.563	0.575		
Molecule		N1	C2	C5	C6
Alloxan	−2243.02269	7.966	4.961	5.702	5.102
		O2	O5	O6	H1
		8.559	8.456	8.611	0.482
Guanidine	−1870.54121	N1	N2	N3	C
HCO_3		7.942	7.916	7.972	5.034
		H1	H2	H3	H4
		0.527	0.564	0.600	0.528
		H5	H6	O1	O2
		0.547	0.543	8.799	8.738
		O3	C2	H	
		8.819	4.994	0.478	

Table 8. Melamine results.

Melamine nuclear quadrupole coupling parameters (MHz)[a].

N Basis	Site	χ_R	χ_T	χ_π	η
344	NH_2	+ 1.2796	+ 2.8159	− 4.0955	0.460
	Ring N	+ 1.1158	+ 2.2459	− 3.3627	0.336
NQR	NH_2	(+)0.9192	(+)2.3578	(−)3.2770	0.439
	Ring	(+)0.1247	(+)2.4429	(−)2.5676	0.903

[a] Total energy −1774.65008 a.u.; Mulliken populations N1, C2, N(H_2), H 7.712, 5.204, 7.946, 0.569 e, respectively.

3.6 Guanidine Bicarbonate and Related Ions

The NQR spectra of a number of guanidine salts have been recorded [55, 56]. With a few exceptions, the cation yields a NQCC χ_{zz} of 3.554 MHz, with asymmetry η 0.3949 [55]. A survey of the known crystal structures showed that only the bicarbonate fulfilled the requirement to have a small enough number of atoms in the unit cell to be a practicable possibility for lattice calculation (Fig. 7) [57]; with 60 atoms per cell and 344 GTOs for a 6-31G (C, N)/4-31G(H) basis for the cation, a minimal basis for the bicarbonate anion was practicable. The NH bonds are short in this X-ray structure. Because of the lack of full 3-fold symmetry in the X-ray structure, the tensor elements at each of the N atoms are slightly variable. However, there is no doubt that the principal value χ_{zz} lies perpendicular to the CNH_2 skeleton, i.e. it is a local χ_π value, as has been assumed previously [55]. The smallest element lies along the external bisector of the HNH angle, i.e. in-plane and perpendicular to the CN bond. The rather high value for χ_{zz} is probably a result of the rather compressed NH bonds used from the X-ray structure. The Mulliken analysis for guanidine bicarbonate shows the latter anion to have a net charge of 0.83 e, while most of the positive charge is localised on the central C atom of the guanidine moiety. Thus, as in the other heterocycles of this group, the N atoms are strongly negatively charged (Table 7).

3.7 Melamine

Recently, the NQR spectrum of melamine has yielded a number of new lines, making a full assignment possible for the two N centres [58]. The neutron diffraction structure [59] with 60 atoms had 372 AOs per cell with the 6-31G (C, N)/4-31G (H) basis. At the amino centres, we find (Table 8) the expected direction of χ_{zz} is out-of-plane to the local CNH_2 group, while

χ_{yy} lies along the CN bond. At the ring N atoms, the value of χ_{zz} is found to be χ_{π}, which is somewhat unexpected, with the in-plane element being χ_{yy}. Further study of this system, with a larger basis set is clearly justified.

4. Conclusions

The choice of a cluster to represent a lattice has always been an approximation. The legitimacy of the approach will depend upon how well the cluster represents the nearest neighbours; given that the EFG declines with r^{-3}, it is common for the approach to succeed; however, size limitations in all computer programmes will inevitably restrict the size of the cluster; thus difficult choises have to be made over the range of interactions possible. The present study of thiourea showed this problem directly, with unbalanced clusters leading to unacceptable results, even though the case for inclusion of the extra neighbours could be made. A further point is that with organic systems especially, the clusters lack symmetry, and hence are very costly in cpu time and generate large electron repulsion integral files.

The use of programmes such as CRYSTAL-92 make possible the assignment of a number of systems where the small cluster approach is inappropriate and add an additional element of rigor. By making use of the higher symmetry of the crystal and the repeating unit, the lattice calculation can be faster than that of the cluster. This is at the expense of generating large electron repulsion files. Prototype studies with a direct-scf module, where the integrals are recomputed for each element of the scf matrix, shows that the problem is not insuperable, but uses much longer cpu times for the (wasted) recomputations required. In order to keep the files to the smallest possible size in the present study with the conventional scf module, we made use of the Pople-style basis sets, and in particular the 6-31G (for C, N, O) with 4-31G(H) and 66-31G (for S). These bases do not have sufficient flexibility in radial component of the GTO to give confidence in assignment of two calculated EFG tensor elements which have similar magnitudes. However they do allow an extension of our previous cluster studies to a more diverse group of molecules, and do not have the problems associated with the choice of cluster size and possible edge effects. It appears that for many molecules containing only C, N, O and H, that the Dunning contraction of the Huzinaga 9s5p/5s bases can be used in CRYSTAL-92, although the authors specifically advise against this. The result can be numerical instability in some cases, with consequent failure to achieve an SCF convergence; but in our hands, the limiting factor on the use of these DZ bases is often only the increased CPU time and extra 2-electron integral filespace utilised.

In the cases where both cluster and lattice calculations were studied, the results were surprisingly close. It is clear that one shell of nearest neighbours is sufficient to generate most of the EFG at the test centre arising from the bulk; indeed the largest effects are within the molecule under consideration, except where H-bonding is important.

All of the amide-like molecules studied here have very similar quadrupole coupling patterns. Thus for uracil, alloxan and parabanic acid, the principal value χ_{zz} is always out-of-plane, while χ_{xx} lies close to the NH bond. The use of X-ray structures, in contrast to neutron diffraction, produces a number of problems with imprecision in the heavy atom positions leading to lack of symmetry in molecules where local molecular symmetry might be expected on the basis of solution and other data. There seems a case for carrying out a local averaging of the X-ray coordinates prior to the EFG calculation. This is even more necessary for the H-atom positions from X-ray analyses; the HN and HC are normally shortened by up to 0.1–0.2 Å, and this will introduce an error with the computed EFG, if not corrected in advance. On the other hand, it is possible that such idealisation will in itself produce an error in some cases. Where practicable it is appropriate to attempt some optimization of the NH length, and CRYSTAL-92 does offer this facility.

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