Quadrupole Coupling in Purines and Pyrimidines by Hartree-Fock Lattice Calculations of Electric Field Gradients*

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Z. Naturforsch. **51 a,** 479–488 (1996); received January 5, 1996

We present *ab initio* Hartree-Fock lattice calculations on adenine, guanine and hypoxanthine, and some pyrimidines, including cytosine and uracil derivatives. The electric field gradients at the nitrogen centres are related to NQR experimental determinations of nuclear quadrupole coupling constants. The calculations were performed as lattice calculations in the unit cell environment, with 6-31G or double zeta basis sets at the SCF level. The present analysis strongly suggests that χ_{zz} at N_3 in cytosine, N_3 in guanine are both positive, and approximately tangential to the ring at that centre. In contrast, N_7 in guanine is like most other azine-type N centres, with a largely radial direction for χ_{zz}. The 3-protonated cytosine ring has χ_{zz} as the local π-direction.

Introduction

We have recently given a number of results of *ab initio* Hartree-Fock lattice calculations [1 - 3] in which the electric field gradient (EFG) tensor elements (q_{ii}) are related to the nuclear quadrupole coupling constants (NQCC, χ_{ii}) obtained by microwave spectroscopy (MW) of the vapour, or NQR of the polycrystalline solid [4, 5]. The relationship between the EFG and NQCC is shown in the equation

$$\chi_{ii} = e^2 Q_Z q_{ii} / h a_0^3 = 234.96\, Q_Z q_{ii}, \qquad (1)$$

where Q_Z is the relevant atomic quadrupole coupling constant. Values for these with the common nuclei ^{14}N and ^{2}H are well known [6]. The principal EFG element is shown in the equation

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

where there are also elements by cyclic permutation of x, y, z; off-diagonal elements (e. g. with operator xy/r^5) have been removed by diagonalisation.

Other factors connecting the EFG and NQCC with experiment are shown in the equations

$$|\chi_{zz}| \geq |\chi_{yy}| \geq |\chi_{xx}| \qquad (3)$$

(a standard convention adopted here) and

$$\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}, \qquad (4)$$

where the asymmetry parameter (η) is defined.

The present paper extends our recent *ab initio* Hartree-Fock SCF calculations to new systems; for a more detailed background cf. [4] and [5]. The new results used **'CRYSTAL-92'**, SCF programme for periodic systems [7 - 9], and the EFG's were evaluated from the final wave-function by use of the full operator(s) shown above. An important objective of the present study is to determine the signs of the quadrupole coupling. For the present series of compounds, this has rarely been discussed; similarly, the directions of the tensor elements have been uncertain.

1. Basis sets

In view of the large size of the molecules and lattice cell size, we normally used the Pople 6-31G basis, which is very efficient in the **CRYSTAL-92** programme [10], owing to the constraint of s- and p-orbitals to the same radial functions. However, we have found these bases inferior to double zeta (DZ) ones with independent s,p-functions. In some cases, the 6-31G were of the maximum size possible with current programme limitations. In other cases convergence difficulties prevented use of the DZ sets. Hence, where possible we used Huzinaga/Dunning double zeta (DZ) [11, 12] bases for these lattice calculations.

* Presented at the XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA, July 23-28, 1995.

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0932-0784 / 96 / 0500-0479 $ 06.00

In some cases, molecular calculations were carried out with the **GAMESS-UK** suite of programmes.

The lattice calculations, under all circumstances, produced large files of electron repulsion integrals(in excess of 10Gb), making storage of these impossible. Hence **'direct-scf'** calculations were performed, in which the Fock matrix was computed directly. 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. All of the compounds were studied at the crystal structures, with preference for neutron diffraction ones; where these are not available, the C–H and N–H bond lengths were set to 1.085 and 1.020Å; this was unnecessary for the neutron diffraction strutures.

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

We use the 'best' values for both Q_N and Q_H [6]. However, for relatively small bases such as DZ or 6-31G, there is a strong case for treating the value of Q_N as a scaling parameter; this was previously done with our DZ results [1], using a correlation of EFG (q_{ii}) against χ_{ii} from microwave data, to evaluate the appropriate Q_N. The scaled DZ ^{14}N correlation constant was 3.5244 MHz / a. u. (15.000 mb), to be compared with the 'best' value for Q_N of 20.1 mb; we have insufficient material to obtain a scaled value for Q_H so we use the 'best' value (2.860 mb) [6], where 1 barn = 10^{-28} m^2 = 100 fm^2.

2. Results

The cell data for the molecules studied are shown in Table 1, the EFG in Table 2, the derived NQCC and a comparison with NQR data in Table 3; the Mulliken populations in Table 4 are 6-31G except where stated otherwise. 6-31G is the only basis set capable of use through the whole series. The molecules are all different in type and are discussed individually. In some cases, we have partitioned the total atomic populations into bond contributions; these are shown for particular cases in the Figures. In the following discussion, since all the molecules are planar, we have a σ/π separation; the local EFG tensor elements for these cyclic structures are largely radial and tangential (R and T), leading to χ_π, χ_R, and χ_T. It is apparent from the NQR literature cited below for a number of NH bonded groups, where more than one NH occurs in the molecule, that assignments to particular sites are provisional at best; in general no evidence has been presented, and insufficient variations in structure are available to use substituent effects.

Table 1. Lattice calculation data for Pyrimidines and Purines.

System	Basis Set	AO's per cell	Cell symmetry	Total Energy/a.u.
Uracil	6-31G	320	$P2_1/a$	–1648.8736
1,3-Dimethyl-uracil	6-31G	424	$P2_1/c$	–1961.0456
2-Thiouracil	6-31G	178	P_{-1}	–1469.9113
2,4-Dithiouracil	6-31G	392	$P2_1/c$	–4230.4249
1-Methyl-4-thiouracil	6-31G	408	$P2_1/c$	–3095.7732
Cytosine	6-31G	328	$P2_12_12_1$	–1569.8326
Cytosine	DZ	360	$P2_12_12_1$	–1569.2996
Cytosine HCl	6-31G	352	$P2_1/N$	–1631.0435
1-Methylcytosine HI/H_2O	DZ	456	P_{-1}	–1900.5890
Guanine 1H_2O	6-31G	480	$P2_1/c$	–2457.7301
Hypoxanthine	6-31G	392	P_{-1}	–1936.5045
Adenine 3H_2O	6-31G	274	P_{-1}	–1382.2341
Adenine 3H_2O	DZ	300	P_{-1}	–1381.9974
Cytosine	6-31G(opt)		Molecule	–392.43746
Cytosine	DZ+MP2(opt)		Molecule	–393.36370
Cytosine Cation	6-31G(opt)		Molecule	–392.83205
Cytosine Cation	DZ+MP2(opt)		Molecule	–393.74350

2.1. Uracils

Uracil [13] itself has space group $P2_1/a$ (Table1), whereas the 1,3-dimethyl- [14], 1-methyl-4-thio- [15], and 2,4-dithio-uracils [16] are all $P2_1/c$, giving a total of 300 - 400 AO's per cell. Owing to the lower symmetry, 2-thiouracil (P_{-1}) [17] has only 178 AO's per cell.

Each of the simple uracils show [18 - 21] very similar NQCC at N_1 and N_3 for the cases where the 2- and 4-groups are similar (Table 3; **3b**, **3c**, **3e**). The NQR experiment does yield slightly differing asymmetry parameters for the centres N_1 and N_3 in these circumstances, and they are chemically distinct; however, neither the NQR data nor the calculations are sufficiently precise to allow any differentiation of the sites.In contrast, when the 2- and 4-groups are different [20] (Table 3; **3d**) or the 1- and 3-groups differ, then the calculations do distinguish the sites, and in the former case there is very close agreement with the NQR data. In this group of compounds **3a-3e**, all except 1,3-dimethyluracil(**3b**) have H-bonded lattices; hence the dimethyl-compound is a good case

Table 2. Electric Field Gradients for Pyrimidines and Purines.

Centre	Basis set	q_{zz}	q_{yy}	q_{xx}	η
2a) Uracil					
N_1H	6-31G	-0.6623	+0.5460	+0.1163	0.649
N_3H	6-31G	-0.6562	+0.5427	+0.1135	0.654
2b) 1,3-Dimethyluracil					
N_1Me	6-31G	-0.6718	+0.3989	+0.2729	0.188
N_3Me	6-31G	-0.6806	+0.3142	+0.2663	0.217
2c) 2-Thiouracil					
N_1H	6-31G	-0.5654	+0.4267	+0.1386	0.510
N_3H	6-31G	-0.5586	+0.4847	+0.0739	0.735
2d) 2,4-Dithiouracil					
N_1H	6-31G	-0.5722	+0.4479	+0.1244	0.565
N_3H	6-31G	-0.5524	+0.4837	+0.0686	0.751
2e) 1-Methyl-4-thiouracil					
N_1Me	6-31G	-0.6284	+0.3718	+0.2566	0.183
N_3H	6-31G	-0.5772	+0.4562	+0.1210	0.581
2f) Cytosine (free base)					
$N_1(H)$	6-31G	-0.5822	+0.4608	+0.1214	0.583
N_3	6-31G	+0.6930	-0.5434	-0.1496	0.568
$N_4(H_2)$	6-31G	-0.8626	+0.5635	+0.2991	0.306
$N_1(H)$	DZ	-0.7328	+0.5960	+0.1368	0.627
N_3	DZ	+0.7999	-0.6723	-0.1277	0.681
$N_4(H_2)$	DZ	-0.9292	+0.6694	+0.2598	0.441
$H_1(N_1)$	DZ	+0.3466	-0.2167	-0.1299	0.250
$H_{4a}(N_4)$	DZ	+0.3780	-0.2241	-0.1539	0.186
$H_{4b}(N_4)$	DZ	+0.3772	-0.2243	-0.1529	0.189
$N_1(H)$	DZ+MP2(opt)	-0.7457(π)	+0.4152(T)	+0.3305(R)	0.114
N_3	DZ+MP2(opt)	-0.7730(R)	+0.6455(T)	+0.1275(π)	0.670
$N_4(H_2)$	DZ+MP2(opt)	-1.0330(π)	+0.6266(R)	+0.4064(T)	0.213
$H_1(N_1)$	DZ+MP2(opt)	+0.4194(R)	-0.2406(π)	-0.1789(T)	0.147
$H_{4a}(N_4)$	DZ+MP2(opt)	+0.4440(R)	-0.2602(π)	-0.1839(T)	0.172
$H_{4b}(N_4)$	DZ+MP2(opt)	+0.4325(R)	-0.2508(π)	-0.1818(T)	0.159
2g) Cytosine HCl					
$N_1(H)$	6-31G	-0.7077	+0.5541	+0.1536	0.566
$N_3(H)$	6-31G	-0.7341	+0.6215	+0.1125	0.693
$N_4(H_2)$	6-31G	-0.7373	+0.5534	+0.1838	0.501
$H_1(N_1)$	6-31G	+0.3307	-0.2085	-0.1233	0.258
$H_3(N_3)$	6-31G	+0.3320	-0.2072	-0.1248	0.248
$H_{4a}(N_4)$	6-31G	+0.3759	-0.2245	-0.1514	0.194
$H_{4b}(N_4)$	6-31G	+0.3685	-0.2129	-0.1555	0.156
2h) Cytosine Protonated					
$N_1(H)$	6-31G	-0.8641(π)	+0.5530(T)	+0.3111(R)	0.280
$N_3(H)$	6-31G	-0.9195(π)	+0.5802(T)	+0.3393(R)	0.262
$N_4(H_2)$	6-31G	-0.9077(π)	+0.6041(T)	+0.3036(R)	0.331
$N_1(H)$	DZ+MP2	-1.0187(π)	+0.6707(T)	+0.3481(R)	0.317
$N_3(H)$	DZ+MP2	-1.0651(π)	+0.6931(T)	+0.3720(R)	0.301
$N_4(H_2)$	DZ+MP2	-1.0651(π)	+0.7483(T)	+0.3168(R)	0.405
$H_1(N_1)$	DZ+MP2	+0.3933(R)	-0.2359(π)	-0.1574(T)	0.199
$H_3(N_3)$	DZ+MP2	+0.3873(R)	-0.2351(π)	-0.1522(T)	0.214
$H_{4a}(N_4)$	DZ+MP2	+0.4093(R)	-0.2439(π)	-0.1654(T)	0.192
$H_{4b}(N_4)$	DZ+MP2	+0.4082(R)	-0.2444(π)	-0.1638(T)	0.197
2i) 1-Methylcytosine Hemi-hydriodide Hemi-hydrate $C_5H_7N_3O_2 + C_5H_8N_3O_2{}^+I^- H_2O$					
$N_{1A}Me$	DZ	-0.9357	0.5107	0.4250	0.092
$N_{1B}Me$	DZ	-0.9491	0.5891	0.3600	0.241
N_{3A}	DZ	+0.8209	-0.6608	-0.1601	0.610
N_{3B}	DZ	-0.8554	+0.7279	+0.1275	0.702
$N_{4A}H_2$	DZ	-0.8761	+0.6640	+0.2121	0.521
$N_{4B}H_2$	DZ	-0.6900	+0.6719	+0.0180	0.948
2j) Guanine Monohydrate					
N_1H	6-31G	-0.7712	+0.6246	+0.1467	0.620
N_3	6-31G	+0.7543	-0.5224	-0.2319	0.385
N_7	6-31G	-0.7806	+0.5053	+0.2753	0.295
N_9H	6-31G	-0.6225	+0.4892	+0.1333	0.572
N_2H_2	6-31G	-0.8999	+0.6859	+0.2141	0.524
H_1N_1	6-31G	+0.3022	-0.1929	-0.1093	0.277
H_9N_9	6-31G	+0.3519	-0.2118	-0.1401	0.204
$H_{2a}N_2$	6-31G	+0.3537	-0.2111	-0.1426	0.194
$H_{2b}N_2$	6-31G	+0.3904	-0.2340	-0.1563	0.199
2k) Hypoxanthine					
$N_{1A}H$	6-31G	-0.4811	+0.4186	+0.0625	0.740
N_{3A}	6-31G	-0.7441	+0.5960	+0.1482	0.602
N_{7A}	6-31G	-0.5735	+0.5340	+0.0395	0.862
$N_{9A}H$	6-31G	-0.4943	+0.4300	+0.0643	0.740
$N_{1B}H$	6-31G	-0.4873	+0.4028	+0.0845	0.653
N_{3B}	6-31G	-0.7427	+0.6161	+0.0743	0.730
N_{7B}	6-31G	-0.6131	+0.5473	+0.0658	0.785
$N_{9B}H$	6-31G	-0.5084	+0.4260	+0.0824	0.676
2l) Adenine Trihydrate					
N_1	6-31G	-0.8067	0.6779	0.1288	0.681
N_1	DZ	-0.9954	0.7612	0.2343	0.529
N_3	6-31G	-0.7791	0.5505	0.2286	0.413
N_3	DZ	-0.9622	0.5866	0.3756	0.219
N_7	6-31G	-0.9612	0.5714	0.3898	0.189
N_7	DZ	-1.1786	0.6205	0.5581	0.053
N_9H	6-31G	-0.5845	0.5520	0.0625	0.786
N_9H	DZ	-0.6675	0.6321	0.0354	0.894
6-NH_2	6-31G	0.4559	-0.4063	-0.0496	0.782
6-NH_2	DZ	0.4212	-0.4171	-0.0104	0.601

to observe the intrinsic properties of the uracil system. The present data support the N_1H and N_3H order proposed previously [19]. A 2-thio-substituent raises the asymmety parameter considerably at both N_1 and N_3, but the case which would be most important is 4-thiouracil, where the change at the non-adjacent N_1 is of interest. So far there appears to be no crystal structure for 4-thiouracil.

Table 3. Derived ^{14}N NQCC for Pyrimidines and Purines.

Centre	Method	χ_{zz}	χ_{yy}	χ_{xx}	η
3a) Uracil					
N_1H	6-31G	-3.144	+2.592	+0.552	0.649
N_3H	6-31G	-3.114	+2.576	+0.539	0.654
N_1H	NQR [19]	(-)2.627	(+)2.014	(+)0.613	0.533
N_3H	NQR [19]	(-)2.583	(+)1.986	(+)0.596	0.538
3b) 1,3-Dimethyluracil					
N_1Me	6-31G	-3.189	+1.893	+1.295	0.188
N_3Me	6-31G	-3.214	+1.484	+1.258	0.217
N_1Me	NQR [19]	(-)3.337	+1.790	+1.547	0.073
N_3Me	NQR [19]	(-)3.258	+1.808	+1.450	0.110
3c) 2-Thiouracil					
N_1H	6-31G	-2.760	+2.015	+0.646	0.510
N_3H	6-31G	-2.638	+2.289	+0.349	0.735
N_1H	NQR [20]	2.360	1.864	0.496	0.580
N_3H	NQR [20]	2.207	1.913	0.294	0.734
3d) 2,4-Dithiouracil					
N_1H	6-31G	-2.702	+2.115	+0.588	0.565
N_3H	6-31G	-2.609	+2.284	+0.324	0.751
N_1H	NQR [20]	(-)2.140	1.800	0.340	0.682
N_3H	NQR [20]	(-)2.140	1.920	0.220	0.794
3e) 1-Methyl-4-thiouracil					
N_1Me	6-31G	-2.968	+1.756	+1.212	0.183
N_3H	6-31G	-2.726	+2.154	+0.571	0.581
3f) Cytosine (free base)					
N_1H	6-31G	-2.750(π)	+2.176(T)	+0.573(R)	0.583
$N_1(H)$	DZ+MP2(opt)	-3.522(π)	+1.961(T)	+1.561(R)	0.114
N_1H	NQR [21]	(-)3.410	(+)2.039	(+)1.379	0.196
N_1H	NQR [24]	(-)2.180	(+)1.852	(+)0.328	0.699
N_3	6-31G	+3.289(T)	-2.579(R)	-0.710(π)	0.568
N_3	DZ+MP2(opt)	-3.561(R)	+3.049(T)	+0.602(π)	0.670
N_3	NQR [21]	2.160	1.900	0.260	0.759
N_3	NQR [24]	2.865	2.558	0.307	0.786
N_4H_2	6-31G	-4.094(R)	+2.674(π)	+1.420(T)	0.306
$N_4(H_2)$	DZ+MP2(opt)	-4.879(π)	+2.959(R)	+1.919(T)	0.213
N_4H_2	NQR [21]	2.933	2.037	0.896	0.389
N_4H_2	NQR [24]	2.961	2.019	0.942	0.364
3g) Cytosine (HBr salt)					
N_1H	NQR [24]	2.449	1.981	0.468	0.618
N_3H	NQR [24]	2.601	2.171	0.430	0.669
N_4H_2	NQR [24]	2.494	1.910	0.584	0.532
3h) Cytosine (HCl salt)					
N_1H	6-31G	-3.342(π)	+2.617(T)	+0.725(R)	0.566
N_1H	NQR [24]	2.448	1.982	0.466	0.619
N_1H	NQR [25]	2.414	1.818	0.596	0.506
N_3H	6-31G	-3.467(π)	+2.935(T)	+0.532(R)	0.693
N_3H	NQR [24]	2.507	2.201	0.306	0.756
N_3H	NQR [25]	2.514	2.226	0.288	0.771
N_4H_2	6-31G	-3.482(π)	+2.614(T)	+0.868(R)	0.501
N_4H_2	NQR [24]	2.527	1.917	0.610	0.517
N_4H_2	NQR [25]	2.599	1.896	0.618	0.508
3i) Cytosine Protonated					
$N_1(H)$	DZ+MP2	-4.811(π)	+3.168(T)	+1.644(R)	0.317
$N_3(H)$	DZ+MP2	-5.030(π)	+3.273(T)	+1.757(R)	0.301
$N_4(H_2)$	DZ+MP2	-5.030(π)	+3.534(T)	+1.496(R)	0.405
3j) 1-Methylcytosine Hemi-hydriodide Hemi-hydrate $C_5H_7N_3O_2$(A) + $C_5H_8N_3O_2$(B) I H_2O					
$N_{1A}Me$	DZ	-4.419	2.412	2.007	0.092
$N_{1A}Me$	DZ(scaled)	-3.297	1.800	1.498	0.092
$N_{1B}Me$	DZ	-4.482	2.782	1.700	0.241
$N_{1B}Me$	DZ(scaled)	-3.345	2.076	1.269	0.241
N_{3A}	DZ	+3.877	-3.121	-0.756	0.610
N_{3A}	DZ(scaled)	+2.893	-2.329	-0.564	0.610
N_{3A}	NQR [25]	2.666	2.602	0.063	0.953
$N_{3B}H$	DZ	-4.040	+3.443	+0.606	0.702
$N_{3B}H$	DZ(scaled)	-3.015	+2.566	+0.449	0.702
$N_{3B}H$	NQR [25]	1.947	1.834	0.113	0.884
$N_{4A}H_2$	DZ	-4.095	+3.136	+1.002	0.521
$N_{4A}H_2$	DZ(scaled)	-3.056	+2.340	+0.748	0.521
N_{4A}	NQR [25]	2.890	1.996	0.894	0.381
$N_{4B}H_2$	DZ	-3.259	+3.174	+0.085	0.948
$N_{4B}H_2$	DZ(scaled)	-2.432	+2.368	+0.064	0.948
N_{4A}	NQR [25]	2.890	1.996	0.894	0.381
3k) Guanine Monohydrate					
N_1H	6-31G	-3.642	+2.950	+0.693	0.620
N_1H	NQR [24]	2.628	2.108	0.520	0.604
N_3	6-31G	+3.562	-2.467	-1.095	0.385
N_7	6-31G	-3.687	+2.386	+1.300	0.295
N_7	NQR [24]	3.265	1.890	1.375	0.158
N_9H	6-31G	-2.940	+2.310	+0.630	0.572
N_9H	NQR [24]	1.909	1.671	0.238	0.751
N_2H_2	6-31G	-4.250	+3.239	+1.011	0.524
N_2H_2	NQR [24]	3.372	2.468	0.904	0.464
H_1N_1	6-31G	+1.427	-0.911	-0.516	0.277
H_9N_9	6-31G	+1.662	-1.000	-0.662	0.204
$H_{2a}N_2$	6-31G	+1.670	-0.997	-0.673	0.194
$H_{2b}N_2$	6-31G	+1.844	-1.105	-0.738	0.199
3l) Hypoxanthine					
$N_{1A}H$	6-31G	-2.272	+1.976	+0.295	0.740
$N_{1B}H$	6-31G	-2.301	+1.902	+0.399	0.653
$N_{1A}H$	NQR [21]	1.637	1.634	0.003	0.996
N_{3A}	6-31G	-3.514	+2.815	+0.700	0.602
N_{3B}	6-31G	-3.508	+2.910	+0.351	0.730
$N_{3A.B}H$	NQR [21]	3.647	2.113	1.534	0.159
N_{7A}	6-31G	-2.708	+2.522	+0.187	0.862
N_{7B}	6-31G	-2.895	+2.585	+0.311	0.785
$N_{7A.B}H$	NQR [21]	3.187	1.993	1.194	0.251
$N_{9A}H$	6-31G	-2.334	+2.031	+0.304	0.740
$N_{9B}H$	6-31G	-2.401	+2.012	+0.389	0.676
$N_{9A.B}H$	NQR [21]	1.870	1.650	0.220	0.765
3m) Adenine Trihydrate					
N_1	6-31G	-3.829	3.217	0.611	0.681
N_1	DZ	-4.724	3.613	1.112	0.529
N_1	DZ(scaled)	-3.508	2.683	0.826	0.529
N_1	NQR [21]	3.407	2.274	1.133	0.335
N_3	6-31G	-3.698	2.613	1.085	0.413
N_3	DZ	-4.557	2.784	1.783	0.219
N_3	DZ(scaled)	-3.391	2.067	1.324	0.219
N_3	NQR [21]	3.883	2.307	1.577	0.188
N_7	6-31G	-4.562	2.712	1.850	0.189
N_7	DZ	-5.594	2.945	2.649	0.053
N_7	DZ(scaled)	-4.154	2.187	1.967	0.053
N_7	NQR [21]	3.203	1.946	1.257	0.215
N_9H	6-31G	-2.774	2.478	0.297	0.786
N_9H	DZ	-3.168	3.000	0.168	0.894
N_9H	DZ(scaled)	-2.353	2.228	0.125	0.894
N_9H	NQR [21]	1.990	1.680	0.310	0.688
N_6H_2	6-31G	2.164	-1.928	-0.235	0.782
N_6H_2	DZ	2.474	-1.980	-0.049	0.601
N_6H_2	DZ(scaled)	1.837	-1.470	-0.037	0.601
N_6H_2	NQR [21]	2.843	2.087	0.756	0.468

Table 4. Atomic Populations for Pyrimidines and Purines.

4a) Uracil

N_1	C_2	O_2	N_3	C_4	O_4	C_5	C_6	H_1	H_3	H_5	H_6
7.851	5.010	8.627	7.916	5.153	8.751	6.488	5.690	0.701	0.663	0.593	0.556

4b) 1,3-Dimethyluracil

N_1	C_2	O_2	N_3	C_4	O_4	C_5	C_6	C_1	H_{1-Me}	C_3	H_{3-Me}	H_5	H_6
7.608	5.094	8.715	7.651	5.270	8.779	6.249	5.838	6.173	0.820	6.183	0.818	0.769	0.757

4c) 2-Thiouracil

N_1	C_2	S_2	N_3	C_4	O_4	C_5	C_6	H_1	H_3	H_5	H_6
7.222	5.318	16.482	7.793	5.257	8.753	6.227	5.808	0.616	0.506	0.736	0.780

4d) 2,4-Dithiouracil

N_1	C_2	S_2	N_3	C_4	S_4	C_5	C_6	H_1	H_3	H_5	H_6
7.725	5.322	16.436	7.726	5.560	16.475	6.222	5.770	0.619	0.600	0.787	0.758

4e) 1-Methyl-4-dithiouracil

N_1	C_2	O_2	N_3	C_4	S_4	C_5	C_6	C_1	H_{Me}	H_{N_3}	H_5	H_6
7.624	5.069	8.708	7.746	5.522	16.523	6.208	5.789	6.167	0.823	0.622	0.771	0.782

4f) Cytosine (free base)

Basis	N_1	C_2	O_2	N_3	C_4	N_4	C_5	C_6	H_1	H_{4a}	H_{4b}	H_5	H_6
6-31G	7.905	5.017	8.791	7.824	5.283	7.988	6.454	5.775	0.492	0.558	0.538	0.689	0.688
6-31G(opt)	7.960	5.093	8.598	7.671	5.354	7.947	6.304	5.737	0.590	0.622	0.598	0.775	0.751
dz+mp2(opt)	7.509	5.822	8.291	7.158	5.712	7.730	6.226	5.990	0.637	0.663	0.640	0.824	0.797
dz+mp2(π)	1.627	0.922	1.434	1.243	0.910	1.773	1.120	0.970	0.000	0.000	0.000	0.000	0.000

4g) Cytosine HCl

Basis	N_1	C_2	O_2	N_3	C_4	N_4	C_5	C_6	H_1	H_3	H_{4a}	H_{4b}	H_5	H_6
6-31G	7.991	4.911	8.697	8.005	5.107	7.924	6.467	5.703	0.465	0.611	0.606	0.566	0.655	0.635

4h)Cytosine 3-protonated(equilibrium)

Basis	N_1	C_2	O_2	N_3	C_4	N_4	C_5	C_6	H_1	H_3	H_{4a}	H_{4b}	H_5	H_6
6-31G	7.964	4.929	8.472	8.050	5.054	7.935	6.329	5.681	0.536	0.543	0.557	0.568	0.704	0.681
dz+mp2(opt)	7.483	5.639	8.194	7.531	5.461	7.685	6.180	5.957	0.576	0.589	0.594	0.607	0.764	0.739
dz+mp2(π)	1.610	0.898	1.385	1.624	0.834	1.662	1.106	0.881	0.000	0.000	0.000	0.000	0.000	0.000

4i) 1-Methylcytosine Hemi-hydriodide Hemi-hydrate

N_{1A}	C_{2A}	O_{2A}	N_{3A}	C_{4A}	N_{4A}	C_{5A}	C_{6A}	$C_{Me.A}$	$H_{Me.A}$	$H_{4A}(NH_2)$	H_{5A}	H_{6A}	Total A	Total H_2O	I^-
7.451	5.380	8.596	7.575	5.516	7.888	6.390	6.011	6.451	2.289	1.155	0.679	0.718	66.099	10.125	7.677
N_{1B}	C_{2B}	O_{2B}	N_{3B}	C_{4B}	N_{4B}	C_{5B}	C_{6B}	$C_{Me.B}$	$H_{Me.B}$	$H_{4B}(NH_2)$	H_{5B}	H_{6B}	H_{3B}	Total B	
7.502	5.309	8.538	7.770	5.344	7.911	6.378	5.839	6.485	2.242	0.959	0.721	0.717	0.384	66.099	

4j) Guanine $1H_2O$

N_1	C_2	N_2	N_3	C_4	C_5	C_6	O_6	N_7	C_8	N_9	H_1	H_{2a}	H_{H2b}	H_8	H_9
8.086	4.947	8.025	7.754	5.273	6.093	5.004	8.763	7.710	5.640	8.005	0.452	0.554	0.525	0.704	0.472

4k) Hypoxanthine(molecule A)

N_1	C_2	N_3	C_4	C_5	C_6	O_6	N_7	C_8	N_9	H_1	H_2	H_8	H_9
7.933	5.626	7.554	5.451	6.031	5.024	8.783	7.711	5.601	7.937	0.491	0.691	0.680	0.484

4l) Adenine $3H_2O$

Basis	N_1	C_2	N_3	C_4	C_5	C_6	N_7	C_8	N_9	H_2	H_8	H_9	N_4	H_{4a}	H_{4b}
dz	7.309	6.190	7.243	5.629	5.946	5.549	7.170	5.898	7.692	0.691	0.691	0.415	7.836	0.484	0.492
6-31G	7.602	5.772	7.541	5.315	6.059	5.251	7.439	5.513	7.925	0.702	0.665	0.448	7.883	0.504	0.512

The atomic populations (Table 4) show very high polarisation of all bonds, a characteristic of the 6-31G basis set; the DZ/SCF and DZ/MP2 correlated wavefunctions produce smaller bond dipoles (Figures 1 to 6), obtained by summing the charges around centres, but the principal effects are similar to 6-31G, so that discussion of the latter is justified. Comparison of uracil with its 1,3-dimethyl-derivative (Figs. 1 and 2) shows that replacement of H by Me leads to an increase in electron donation to N (from about 0.33 to nearly 0.4 e); in consequence the N–CO bonds are less polarised in the NMe compound, and the CO dipoles are increased. The 1-Me group also has a marked effect on the C_5HC_6H unit; the reduction in electron flow to N_1Me from C_6 leads to much lower polarity of the C_5HC_6H unit. Exchange of H by Me is primarily a σ-bond effect. These changes around the N atoms whose environment is now 3 C atoms, reduces the asymmetry parameter substantially. This occurs mainly by averaging the values of χ_{yy} and χ_{xx}, which would occur totally in a D_{3h} environment.

2,4-Dithiouracil has all bonds polarised in the same direction as uracil itself (compare Figs. 1 and 3). Although the polarisation of the 4-CX (X = O, S) group

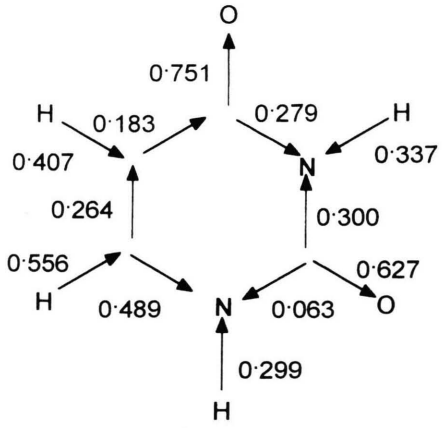

Fig. 1. Bond populations for Uracil with the 6-31G basis set.

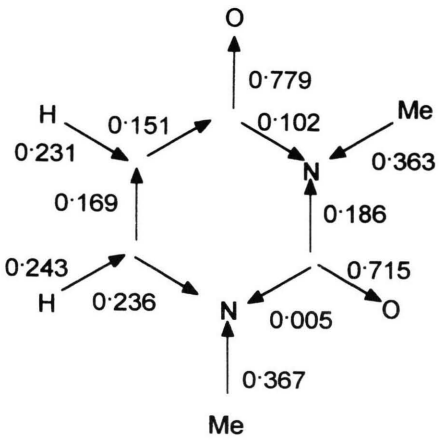

Fig. 2. Bond populations for 1,3-Dimethyluracil with the 6-31G basis set.

is higher than 2-CX in each compound, the dipoles on CS are reduced by about 30% relative to CO. Other major changes are the reduction in dipole on the C_6N_1, C_4N_3 and the C_2N_3 bonds in the X=S case.

2.2. *Cytosines*

2.2.1. Cytosine free base

The crystal structure of cytosine ($P2_12_12_1$) shows [22] a strongly H-bonded lattice with N_3 (of azine-type) weakly bonded to H in another HN_1 at a distance of 1.86 Å; similarly, both H-atoms attached to the C_4NH_2 group are H-bonded to the C_2O oxygen atoms at about 2.00 Å. A number of authors have investigated this system, both in the neutral [18, 23,

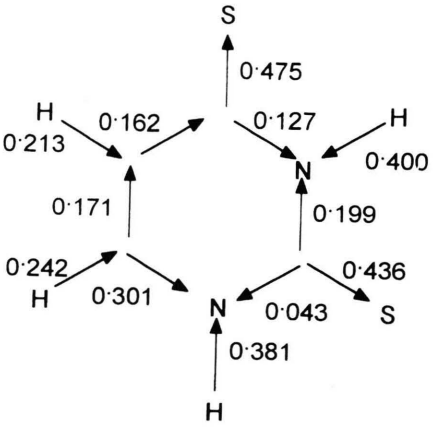

Fig. 3. Bond populations for 2,4-Dithiouracil with the 6-31G basis set.

24] and protonated [24 - 26] forms. Some workers [18, 23] had difficulty with the resonances for one centre, assumed on the basis of comparision with nucleoside derivatives [18] to be N_1; the complete set of resonances was subsequently obtained [21], but does not agree well at one centre with another experiment, where the assignment was based on only 2 resonances [24], one of which was not reported by Rabbani et al. [21]. However, on the basis of changes in acid level leading to the protonated form, the experiments yielding only two resonances [24] look more reliable. In [21], the positions N_1 and N_3 are numbered in the reverse order, but identified by the attached H-atom. The agreement between the NQR data [24] and the present calculations leads to a simplification of the spectral interpretation by removing the centre N_1 from further consideration.

The position at N_3 and the 4-NH_2 group are reminiscent of melamine, 2,4,6-triamino-1,3,5-triazine, where the same structural unit occurs [5, 27], and also the purines discussed below. The anticipated large lone-pair (or imine) NQCC (χ_R) at the pyridine-like N is expected to be near –4 to –4.5 MHz; when there are adjacent NH_2 groups, as here, this does not occur [27]; the magnitude is much reduced. In part, this must be a result of H-bonding present in the amino-compounds but absent in the azine. Further examples are found by comparison of simple pyrimidines with 2-aminopyrimidine [28]. In the melamine calculation [5], χ_{zz} was calculated about 1MHz too large (but negative) at both ring and NH_2 centres. The present calculations used two basis sets, and the results appear similar, but again high. The results are in general

agreement with the assignments of both NQR investigations [21, 24]. However, the sign of χ_{zz} at N_3 is *positive* with both 6-31G and DZ bases, with the z-axis being the local tangential (T) axis; this implies a strong reduction of χ_R in these circumstances, and a switch of direction in χ_{zz} and χ_{yy} relative to a separate lone-pair (χ_R). The 'free' molecule of cytosine has χ_{zz} negative at N_3, so the switch in axes is a result of the neighbours to N_1 and N_3 in the lattice. A similar effect occurs with the azoles, such as imidazole [29]. The present assignment for N_3 in cytosine is a reversal of χ_{zz} and χ_{yy} relative to the assignment by Garcia and Smith [24].

The atomic populations for cytosine, when converted to the local bond dipoles for the 6-31G/SCF and DZ/MP2 calculations (Figs. 4 and 5) show mainly similar polarisation of bonds, but the more rigorous calculation does suggest that N_3 is only an electron acceptor from C_4. The 6-31G/SCF optimised molecular structure (not shown) is very similar to the lattice one (Figure 4).

2.2.2. Cytosine Hydrochloride

A number of crystal structures of cytosine salts are known, but the simplest where NQR data are also known, is the hydrochloride [30]. The structure is $P2_1/N$, leading to 352 AO's per unit cell. The NQR data for the hydrochloride and hydrobromide are very similar, and it seems probable that the same assignments will apply. It is helpful to consider the DZ+MP2 optimized structures for the free base and 3H-protonated forms of cytosine first. On a relative basis, protonation at N_3 leads to a rise in asymmetry at N_1, and also an increase in magnitude for χ_π and χ_T; at N_3, protonation is accompanied by a drop in η and an increase in χ_{zz}, this time with a switch of the π and R axes. This is readily understandable in terms of the similarity of N_1H and N_3H when in the protonated form with the corresponding positions in the neutral cytosines. Thus the direction of χ_{zz} at N_3H in cytosine hydrochloride is probably the π-direction, as is that at N_4H_2 in both the neutral and protonated forms.

It is not practicable to extract the local σ- and π-components of the cytosines from the crystal lattice calculations, since the molecules do not lie parallel to a cell axis; on the other hand we can compare the π-electron densities for the free base and 3H-protonated forms from the 'free molecule' calculations. The results (Table 4) show that protonation of N_3 leads to a loss of π-electron density at most centres, especially N_4 and C_6, but that N_3 gains by 0.38 e; the polarisation of the bond in the neutral and cation are shown in Figs. 5 and 6. Hiyama et al. [25] have drawn attention to the anomalously low χ_{zz} at the imino-N atom (N_3) in cytosine and noted that protonation increases this to a more usual level. This was attributed to a high π-electron density in the free base at N_3 [25]. The present work supports the phenomenon, but with the *reverse* reason; namely the *protonated* form has an especially high density at N_3H. Thus the conclusions by Hiyama et al. [25], which were based on the assumption that χ_{zz} is negative at N_3H, are incorrect.

2.2.3. The 1-methylcytosine hemihydriodide hemihydrate

This is more simply described as a dimeric 1-methylcytosine structure, with an unsymmetrical mono-protonation, leading to two distinct ring structures [31]. The P_{-1} space group made a 6-31G basis calculation practicable. The ^{14}N NQR spectrum [25] has not yielded enough lines to enable a full assignment of frequencies, let alone attribution to centres. Thus we discuss the data, as did the authors [25] in the light of changes relative to the free base and protonated forms of cytosine.

The crystal lattice contains 4 pairs (space group P_{-1}) of 4 species, the 'neutral' $C_5H_7N_3O_2$ (A) and 'cationic' species $C_5H_8N_3O_2^+$ (B), an iodide anion, and a water molecule; the Mulliken analyses show that the total charge associated with the 'neutral' and 'cationic' species is identical, with the water molecule nearly neutral and the iodide anion component having only a partial charge of 0.677 e. Thus a considerable level of electron reorganisation occurs on dimer formation. The added 3H-proton has a charge of 0.38 e, and hence has a very weak σ-bond to N_3, even though the atoms are close. The principal differences between corresponding positions in the dimer structure are at N_3, and to a lesser extent also at N_1, which have *higher* population in the 'cation' than the 'neutral'; the reverse effect occurs at the C_2O_2, C_4 , C_6 and the 4-NH_2 groups. Thus the 3H-proton polarises the skeleton of the 'cation' by electron withdrawal from the latter group of sites. There are a number of probable similarities to the cytosine 3H-protonated example above, but owing to the complexity of the wave-function, and the molecules not lying parallel to a crystal face, we could not perform a detailed analysis.

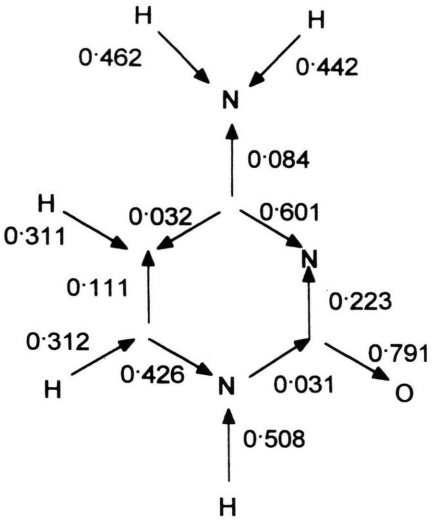

Fig. 4. Bond populations for Cytosine with the 6-31G basis set.

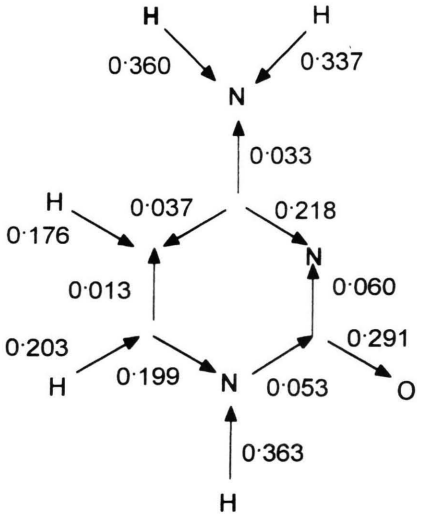

Fig. 5. Bond populations for Cytosine with the DZ+MP2 basis set.

The present calculations indicate near degeneracy of N_1H in molecules A and B, but suggest that the N_4H_2 resonances should be distinct; only one set of resonances has been found for N_4 sites. The $N_{3A}H$ versus $N_{3B}H$ sites, where two assignments have been reported, should have reversed signs for χ_{zz}, as in the cytosine neutral and protonated forms above.

The re-partition of the Mulliken charges into bond populations for cytosine and its 3H-protonated form (Figs. 4 - 6) show a number of interesting features;

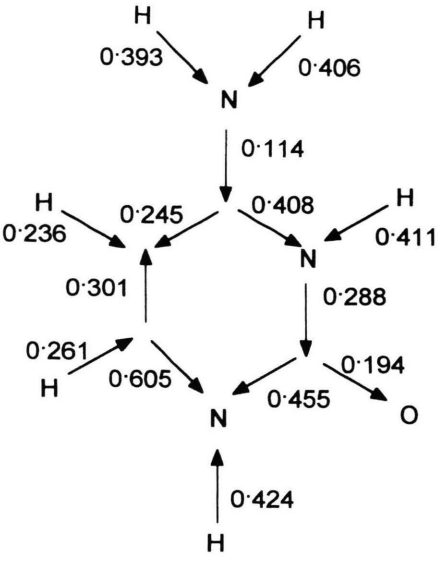

Fig. 6. Bond populations for 3H-Protonated cytosine with the DZ+MP2 basis set.

comparison of Figs. 4 and 5 is a typical case of the 6-31G basis set at the SCF level in contrast to the DZ basis set at the correlated MP2 level; the reduction in charges is marked for the latter case, but (as the directions of the arrows confirm) the dipoles are all in similar directions. Perhaps the most interesting is the protonated species (Fig. 6); the internal dipoles are large, showing the general delocalisation of the positive charge. All the H and C atoms are positive, with the N and O atoms negative; only when the dipoles are summed does the overall net unit charge re-emerge.

2.3. Purines

Double resonance NQR data for several purines such as adenine [18, 21, 24], guanine [23, 24, 32], and hypoxanthine [18, 21, 24, 32] have been obtained. Assignments on the basis of interrelations between these and related compounds, where the 9-HN was replaced by the 9-ribosyl group were given [21]. Thus all 15 resonances for adenine were observed [21], and many of these have been confirmed [24]. Some of these studies also led to ^2H NQCC via the ND and ND_2 compounds obtained by D_2O treatment; in practice, many of these compounds crystallise in hydrated forms, and there is no evidence [21, 24] that the ^{14}N NQCC are changed between the anhydrous and hydrated forms.

The crystal structure of adenine trihydrate [33] has space group P_{-1}; because of the low symmetry for this

large system, a **CRYSTAL-92** calculation on the crystalline system has only 46 atoms per cell; it proved possible to perform calculations at both the 6-31G (274 AO's) and DZ (300 AO's) basis set level. In contrast, hypoxanthine, with the same P_{-1} space group, has two hypoxanthine molecules to the asymmetric uni [34], hence making the lattice calculation much larger. Guanine mono-hydrate, has space group $P2_1/c$, with a water molecule lying on a symmetry axis [35].

For guanine, the full set of NQR frequencies is deficient, in that only one frequency, associated by the authors with the pyridine-like centre N_3 has been obtained [24]. The present results (Table 3) suggest that the general trends above with the 6-31G basis set continue, namely that pyrrole-like centres of NH-type are reasonably well determined, and support the previous conclusions based on comparisons between compounds. Both N_1H and N_9H have high asymmetry parameters. The other principal difference between the centres N_3 and N_7, is that the latter is predicted to be a normal lone-pair centre, with negative value to χ_{zz}, whereas N_3 is predicted to have χ_{zz} *positive*.

The hypoxanthine calculation obtains reasonably good agreement at both N_1H and N_9H, but the asymmetry parameters are much higher at the other centres. In view of the 2 molecules present in the asymmetric unit, upgrading this calculation will be difficult. Adenine follows the same general conclusions for the other purines above; however, the only positive χ_{zz} is that for the 6-amino group. This is unusual and implies a much stronger interaction of the NH_2 group with the ring than is usual.

3. Conclusions

The present study was limited by the use of the 6-31G basis set for most of the lattice systems studied; this is probably the minimum basis set capable of giving some qualitative information on the signs and directions of the EFG tensor elements when compared with NQR data. In the few cases where we have been able to perform DZ basis set calculations, the results are similar; since the latter, with its additional variational freedom through separate radial functions for s and p orbitals, has been relatively successful in our previous work, we think the present study has important new assignments.

There are substantial differences between the calculated and the NQR data for the NQCC at a number of sites in the present series of molecules. The objective of this and related work is to offer an assignment (signs and directions) for the experimentally determined magnitudes. This aspect has not been discussed for the present compounds previously. Except where the asymmetry parameter is high, say above 0.8, the present set of signs is likely to be secure. In this circumstance, deviations of even 20% from the experimental magnitudes are unlikely to be important. The reasons for such discrepancies lie outside the scope of this work; the calculations are constrained by basis set limitations, and to SCF rather than CI calculations; also, the calculated results contain no vibrational effects, in contrast to the experimental data, where vibrational averaging occurs.

The cytosine free base, although much studied by NQR, has now been shown to have χ_{zz} tangential to the ring at N_3; this is unexpected, but seems secure. The effect arises from the electron donation from the 4-amino group effecting the balance at N_3. The amino-azines containing the H_2N–C–N group seem to be worth further study, since the balance of electron density in the strongly π-electron donating NH_2 group, and strongly accepting ring N-atom, lead to a major perturbation of the basic ring system. A similar conclusion with the guanine molecule occurs, whereby χ_{zz} at N_3 is thought to be positive, in contrast to that at N_7, which is negative like so many tertiary N-atoms.

The protonated cytosine ring has a further change of χ_{zz}, which is now in the π-direction at N_3, consistent with notions of resonance in the HN–C–NH cationic moiety.

In general, the NH unit in these systems is better treated by the 6-31G/DZ bases than the tertiary ring N-atoms for this series. Hence, the studies with the purines have had limited success. However, these are the first *ab initio* lattice studies of such compounds. The essential requirement for a high quality crystal structure study is again demonstrated. The necessity to reset the CH and more importantly, NH bond lengths, because of the shortening observed in x-ray crystallography, might be dangerous in some cases; in extreme circumstances, this could determine the accuracy of the predictions of NQCC at such centres. There is a need to be able to optimise the parameters in the structure, with respect to CH and NH bond lengths and directions, while retaining the space group and heavy atom positions. There is a continued case for

the study of individual molecules, as in the present work, (a) with an equilibrium geometry search, (b) with a larger basis set. This could lead to merging of some of the geometric data. The conclusions could then be based on a comparison of the behaviour of the EFG calculations with small and large basis sets on the molecules, followed by comparisons with lattice calculations (which may be at a limiting size with a small basis set).

The Mulliken populations are widely reported as a measure of local charge density and bond polarisation; whilst accepting the limitations, *ab initio* values do not suffer the disadvantage of some more primitive methods in ignoring the overlap populations in the summations. Although the 6-31G and DZ bases show considerable variation, the sense of the bond dipoles is almost always the same, and this offers some confidence that the results are meaningful.

Acknowledgements

It is a pleasure to acknowledge the support of the SERC (now EPSRC) for hardware support, and the **CRYSTAL-92** Group at the Daresbury Laboratory, particularly Drs. V. R. Saunders and N. M. Harrison.

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