The Charge Distribution in Amides and Thioamides by Nuclear Quadrupole Coupling, Dipole Moments and Electronic Structure Calculations*

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The nuclear quadrupole coupling constants from microwave spectroscopy (MW) and quadrupole resonance (NQR) for amides and thioamides are discussed in relation to Hartree-Fock calculations with and without Moller-Plesset correlation effects. The view that the larger dipole moments from thioamides than the corresponding amides is a function of enhanced resonance in the former is discussed and (in effect) confirmed by the present procedures. The principal mechamism seems to be the push/pull π/σ effects of the N atom with respect to the CO and CS groups, with S being a better σ-donor than O; however, the effect is still present with formamidine where no electronegativity effects are important, so the overall effect is the 2,1,1π-electron contribution to the allylic system from N, C, O(S). The use of localised MO's and NO's is described, and the centroid positions are discussed in relation to the polarity of the bonds. The LMO's largely truncate the contributions to each NQCC to the three attached bonds (or 2 bonds + a lone pair orbital at O or S), as is used in the Townes-Dailey procedures. More distant LMO's generally contribute < 0.05 a. u. to the EFG, simplifying the analysis. The effects of O(or S)-protonation of urea and thiourea is discussed.

Introduction

We present a number of new theoretical studies on amides and thioamides using single molecule studies with large basis sets including electron correlation at the MP2 level. These studies concentrate on simple amides and thioamides, and in particular with formamide and thioformamide, acetamide, urea and thiourea and their methylated derivatives. The purpose of the investigation is to reconsider the anomalous ^{14}N quadrupole coupling in these molecules. The background to this matter is as follows. It is generally accepted that the electronegativity of oxygen is greater than that of sulphur; some typical values for elements relevant to the present discussion are: H 2.1, C 2.5 N 3.0, O 3.5 and S 2.5 all from the Pauling scale [1], but other scales exist with similar interrelationships. Each of the above molecules has a ^{14}N centre and either a ^{17}O or ^{33}S centre, all being quadrupolar. The gas phase and solid state ^{14}N nuclear quadrupole coupling constants (NQCC, χ_{ii}) are found by microwave spectroscopy (MW) and nuclear quadrupole resonance (NQR), respectively. The NQCC's are second rank tensors with the conventions

$$|\chi_{zz}| \geq |\chi_{yy}| \geq |\chi_{xx}|, \tag{1}$$

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

in the first defining the magnitude order and the second is the Laplace relationship. χ_{zz} is normally defined as the 'principal' value of the NQCC; we use these conventions here.

The MW data will normally lie in the inertial axis (IA, *ii* = *aa*, *bb*, *cc*) system, requiring a knowledge of the off-diagonal elements χ_{ij} in order to obtain the principal EFG values (*ii* = *xx*, *yy*, *zz*), which are obtained directly in NQR. The principal NQCC (χ_{zz}) at ^{14}N in formamide [2, 3] is -3.848 ± 0.004 MHz while that in thioformamide is thought to be -4.2 ± 0.6 MHz or alternatively -3.7 ± 0.4 MHz [4], a poorly determined comparison. However, the NQCC for urea (-3.51) [5 - 8] is higher than thiourea (-3.12MHz) [9], and this has been attributed to higher resonance in the latter than in the former [10]. It was assumed that the

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higher χ_{zz} at ^{14}N implies higher localisation. These results for amides and thioamides are apparently quite general and have become classic cases for use of the Townes and Dailey analysis with hybrid bonds [10]. We have previously discussed some of the differences between the gas-phase and solid state results for these molecules [11]. The change of phase from gas phase to polycrystalline solids does not change the orientation of the NQCC's [11]. Very detailed investigations of the crystalline field on the actual charge distribution in amides, as opposed to models of the charge, have been reported [12].

The higher electronegativity of O than S should make the amide O a better electron acceptor than S of thioamide [4]. The dipole moments for formamide and thioformamide are 3.71(6) and 4.01(3) D, respectively, [4] with the same dipole moment order in acetamide and thioacetamide from solution measurements [13]. Both imply higher S polarisation than O. Also, ^1H NMR studies for the hindered NH_2 rotation barriers [14, 15] show that the thioamides have higher barriers than the corresponding amide by about 8.5 kJmol^{-1}. However, the NC bonds in gaseous $HCONH_2$ and $HNSNH_2$ are effectively identical in length, implying equal CN bond order [4].

Thus we reconsider the charge distributions in amides and thioamides, ureas and thioureas and their methylated derivatives. In particular we will analyse the contributions to the dipole moment and the electric field gradient (EFG, q_{ij}) tensor and charge distribution on both a molecular orbital set of contributions, and a natural orbital set of increments from the Moller-Plesset (MP2) correlated wave-functions. The MP2 correlation effects are qualitatively similar to the effects of 'singles and doubles CI' (SDCI), but the MP2 studies include (a) *full geometric relaxation* leading to the *correlated equilibrium geometry*, and (b) MP2 includes *all electrons*. In conventional SDCI, the calculation is normally performed as a refinement to a wave-function at the SCF equilibrium geometry, and usually a sub-set of the electrons is included (such as truncation to an all-valence electron set rather than the full set).

1. Methods

The SCF wave-function is a single determinant which consists of a set of doubly occupied molecular orbitals (DOMO's) and virtual MO's (VMO's); each occupied MO pair make a contribution to the total dipole moment (DM) or EFG. Thus by consideration of each MO, we can interpret the effect of the π-electrons separately, hence addressing the question of resonance contributions. A feature of the MP2 calculations is that the overall electronic wave-function (Ψ) is expanded beyond the SCF level (Ψ_0) by further determinants (Ψ_1, etc.) containing 2-electron replacements of the SCF-MO's by the VMO's. The VMO's (the 'anti-bonding' set) play no role in SCF calculations but are included directly in the MP2 calculation as weighted terms through the density matrix. Summation of the contributions for each basis function from all determinants leads to the 'Natural orbitals' (NO's), with properties which can be analysed by electronic population or other methods. Thus the final MP2 natural orbitals contain contributions from all the MO's, but with high occupation numbers from the SCF-MO's and progressively lower contributions from the virtual orbitals (VMO's). As an example of the differences of atomic populations from MO's and NO's, the total π-electrons, strictly 4.000 e for SCF calculations on formamide, become slightly different (usually larger by incorporation of π^* MO's). This leads to some rounding errors in the population analysis below.

All of these studies use the Hartree-Fock Method and involve all electrons in the system under consideration, and the full Hamiltonian operator of the non-relativistic Schrödinger equation is used. The only empirical parameters which are involved are the atomic orbital basis set descussed below. The first stage was to obtain the equilibrium geometry with the basis set and methodology (SCF or MP2); then the dipole moment and EFG components from the resulting wave-functions was evaluated.

The dipole moment components ($\hat{r}$) and EFG tensor elements (q_{ii}, and q_{ij}, where i,j are x, y, or z) are obtained from the electronic wave-function by means of the equations

$$\hat{r} = \langle \Psi_0 \mid r \mid \Psi_0 \rangle, \quad (3)$$

$$q_{zz} = \langle \Psi_0 \mid (3z^2 - r^2) / r^5 \mid \Psi_0 \rangle, \quad (4)$$

$$q_{xy} = \langle \Psi_0 \mid (-3xy / r^5 \mid \Psi_0 \rangle. \quad (5)$$

The nuclear components are *added*, giving the resultant 'total' values for all terms. The EFG's are converted to NQCC's (χ_{ii}) by means of the equation

$$\chi_{ii} = e^2 Q_Z q_{ii} / h a_0^3 = 234.96\, Q_Z q_{ii} \quad (6)$$

Table 1. Equilibrium Structures for Amides and Thioamides[a,b]

Formamide (C_S symmetry)

Bonds (Å)

Method	HC	CO	CN	NH_c	NH_t
DZ/SCF	1.0817	1.2251	1.3609	0.9935	0.9935
TZVP/SCF	1.0911	1.1880	1.3493	0.9925	0.9898
TZVP/MP2	1.0981	1.2158	1.3597	1.0040	1.0015
Microwave[c]	1.098	1.219	1.352	1.0016	1.0015

Angles (°)

Method	HCO	OCN	CNH_c	CNH_t
DZ/SCF	121.72	124.64	120.49	120.49
TZVP/SCF	122.13	125.03	119.42	121.20
TZVP/MP2	122.90	124.87	119.26	121.31
Microwave[c]	122.5	124.7	118.5	120.0

Thioformamide (C_S symmetry)

Bonds (Å)

Method	HC	CS	CN	NH_c	NH_t
DZ/SCF	1.0744	1.6780	1.3410	0.9949	0.9949
TZVP/SCF	1.0788	1.6418	1.3244	0.9926	0.9926
TZVP/MP2	1.0865	1.6379	1.3460	1.0058	1.0038
MWave[d]	1.096	1.6262	1.3582	1.0018	1.0065

Angles (°)

Method	HCS	SCN	CNH_c	CNH_t
DZ/SCF	120.12	126.29	120.85	120.85
TZVP/SCF	120.52	126.41	120.61	120.61
TZVP/MP2	121.87	125.65	119.39	121.54
MWave[d]	126.6	125.3	119.4	120.3

N-Methyl formamide (C_S symmetry)

Bonds (Å)

Method	HC_1	C_1O	C_1N	NH_t	NC_2	C_2H_{ip}	C_2H_{oop}
DZ/SCF	1.0822	1.2290	1.3554	0.9932	1.463	1.0794	1.0804
TZVP/MP2	1.0984	1.2203	1.3552	1.0034	1.4504	1.0848	1.0869

Angles (°)

Method	HCO	OCN	CNH_t	CNC	NCH_{ip}	NCH_{oop}
DZ/SCF	121.55	124.39	118.85	121.68	108.80	110.68
TZVP/MP2	123.05	124.29	118.87	120.88	108.72	110.59

Table 1 (cont).

N,N-Dimethyl formamide (C_S symmetry)

Bonds (Å)

Method	HC	CO	CN	NC_c	NC_t	CH_{ip}	CH_{oop}
DZ/SCF	1.0824	1.2310	1.3534	1.4610	1.4655	1.0798	1.0818
TZVP/MP2	1.0988	1.2231	1.3555	1.4479	1.4522	1.0860	1.0888

Angles (°)

Method	HCO	OCN	CNC_c	CNC_t	NC_cH_{ip}	NC_cH_{oop}
DZ/SCF	121.15	124.52	118.76	121.90	109.55	110.74
TZVP/MP2	122.86	124.49	118.06	122.32	108.99	110.75

Acetamide (C_S symmetry)

Bonds (Å)

Method	$H_{ip}C$	$H_{oop}C$	CC	CO	CN	NH_c	NH_t
DZ/SCF	1.0801	1.0804	1.5131	1.2321	1.3650	0.9946	0.9914
TZVP/SCF	1.0784	1.0845	1.5130	1.1936	1.3563	0.9919	0.9893
TZVP/MP2	1.0876	1.0855	1.5133	1.2209	1.3656	1.0039	1.0006
Elect.Diff.[e]	1.124(av)	1.124(av)	1.519	1.220	1.380	1.022(av)	1.022(av)
Neut.Diff.[f]	1.125	1.119	1.513	1.250	1.337	1.036	1.036
3-21G[f]	1.085	1.080	1.516	1.216	1.358	0.997	0.994

Angles (°)

Method	CCH_{ip}	CCH_{oop}	CCO	OCN	CNH_c	CNH_t
DZ/SCF	112.84	108.87	112.84	121.56	118.59	122.34
TZVP/SCF	109.02	110.35	122.88	122.10	118.60	122.4
TZVP/MP2	112.50	108.95	122.52	122.24	118.25	122.59

Thioacetamide (C_S symmetry)

Bonds (Å)

Method	$H_{ip}C$	$H_{oop}C$	CC	CS	CN	NH_c	NH_t
DZ/SCF	1.0835	1.0792	1.5115	1.6999	1.3421	0.9954	0.9944
TZVP/SCF	1.0849	1.0806	1.5074	1.6603	1.3258	0.9929	0.9915
TZVP/MP2	1.0898	1.0854	1.5088	1.6489	1.3490	1.0051	1.0035

Angles (°)

Method	CCH_{ip}	CCH_{oop}	CCS	SCN	CNH_c	CNH_t
DZ/SCF	111.98	109.60	121.74	122.49	119.60	122.19
TZVP/SCF	111.74	109.33	122.11	122.38	119.20	122.07
TZVP/MP2	111.86	109.64	122.77	122.76	119.04	122.00

Urea (C_{2v})

Bonds (Å)

Method	OC	CN	NH_c	NH_t
DZ/SCF	1.2363	1.3689	0.9926	0.9912
TZVP/SCF	1.1966	1.3606	0.9899	0.9885
TZVP/MP2	1.2194	1.3734	1.0003	0.9997

Angles (°)

Method	OCN	NCN	CNH_c	CNH_t
DZ/SCF	122.03	115.93	117.44	123.31
TZVP/SCF	122.45	115.11	117.37	123.50
TZVP/MP2	122.75	114.50	117.05	123.80

via the appropriate atomic quadrupole moment (Q_Z) for ^{14}N, ^{17}O or ^{33}S, as described below.

1.1. Basis sets and the Atomic Coupling Constants (Q_Z)

The calculations were made with the **GAMESS-UK** programme [16]. We used Huzinaga/Dunning double zeta(DZ) [17, 18] and triple zeta with polarisation (TZVP) bases [19]. These are comparable with our previous work [20, 21] and generally give reliable values for both structural features in the single molecule calculations and the NQCC when compared with MW data. The TZVP basis for C/N/O atoms, for example, contains 20 functions of spd character, with H represented by sp functions. The S atoms had (14s10p) sets from Huzinaga contracted to 7s4p1d. The principal results are shown in Table 1 (molecular equilibrium structural data), Table 2 (energies, dipole moment summaries and Mulliken orbital populations) and Table 4 (NQCC results and comparison with experimental data). More detailed analysis of the molecular orbital (SCF) and natural orbital (MP2) contributions are shown in Tables 3 and 5 for the dipole moment and EFG results. Early studies of this type are shown in [22] and later papers. In order to

Table 1 (cont).

1,3-Dimethylurea (C_{2V})

Bonds (Å)

Method	OC	CN	NH_t	NC_c	CH_{ip}	CH_{oop}
DZ/SCF	1.2402	1.3701	0.9929	1.4609	1.0763	1.0826
TZVP/SCF	1.2005	1.3612	0.9901	1.4459	1.0767	1.0847
TZVP/MP2	1.2245	1.3757	1.0029	1.4468	1.0832	1.0891

Angles (°)

Method	OCN	NCN	CNH_t	CNC_c	NCH_{ip}	NCH_{oop}
DZ/SCF	122.39	115.23	119.42	122.25	108.43	110.81
TZVP/SCF	122.84	114.32	119.25	122.67	108.70	110.86
TZVP/MP2	122.96	114.07	119.67	121.73	107.83	111.05

Tetramethyl urea (C_S)

Bonds (Å)

Method	OC	CN	NC_t	NC_c	CH_{ip}	CH_{oop}
DZ/SCF	1.2528	1.3832	1.4692	1.4775	1.085(ass)	1.085(ass)
TZVP/SCF	1.2094	1.3707	1.4626	1.4562	1.085(ass)	1.085(ass)
TZVP/MP2	CO	CN_1	CN_2	N_1C_{3c}	N_1C_{4t}	N_2C_{5c}
TZVP/MP2	1.2452	1.3868	1.3896	1.4631	1.4540	1.4588
TZVP/MP2	N_2C_{6t}	$C_{4t}H_{ip}$	$C_{4t}H_{oop}$	$C_{5c}H_{ip}$	$C_{5c}H_{oop}$	$C_{4t}H_{ip}$
TZVP/MP2	1.4533	1.0896	1.0906	1.0849	1.0940	1.0782
TZVP/MP2	$C_{4t}H_{oop}$	$C_{6t}H_{oop}$	$C_{6t}H_{ip}$			
TZVP/MP2	1.0942	1.0933	1.0877			

Angles (°)

Method	OCN	NCN	CNC_t	CNC_c	NCH_{ip}	NCH_{oop}
DZ/SCF	116.92	126.23	133.6	116.51	108.5(ass)	108.5(ass)
TZVP/SCF	118.13	123.73	131.21	115.62	108.5(ass)	108.5(ass)

TZVP/MP2	OCN_1	OCN_2	CN_1C_{3c}	CN_1C_{4t}	CN_2C_{5c}
TZVP/MP2	117.57	119.8	113.44	132.80	116.49
TZVP/MP2	CN_2C_{6t}	N_1CN_2	$N_1C_{3c}H_{ip}$	$N_1C_{3c}H_{oop}$	$N_1C_{4t}H_{ip}$
TZVP/MP2	129.32	122.63	107.90	111.05	112.81
TZVP/MP2	$N_1C_{4t}H_{oop}$	$N_2C_{5c}H_{ip}$	$N_2C_{5c}H_{oop}$	$N_2C_{6t}H_{oop}$	$N_2C_{6t}H_{ip}$
TZVP/MP2	110.19	108.77	110.28	112.17	108.40

Thiourea (C_{2V})

Bonds (Å)

Method	SC	CN	NH_c	NH_t
DZ/SCF	1.7254	1.3512	0.9929	0.9942
TZVP/SCF	1.6847	1.3369	0.9915	0.9903
TZVP/MP2	1.6642	1.3574	1.0014	1.0028

Angles (°)

Method	SCN	NCN	CNH_c	CNH_t
DZ/SCF	121.90	116.20	118.19	123.22
TZVP/SCF	121.96	116.07	118.14	122.86
TZVP/MP2	122.61	114.78	117.79	123.17

Table 1 (cont).

Tetramethyl thiourea (C_S)

Bonds (Å)

Method	SC	CN	NC_t	NC_c	CH_{ip}	CH_{oop}
DZ/SCF	1.7733	1.3642	1.4855	1.4810	1.085(ass)	1.085(ass)
TZVP/SCF	1.7227	1.3518	1.4659	1.4692	1.085(ass)	1.085(ass)
TZVP/MP2	CS	CN_1	CN_2	N_1C_{1c}	N_1C_{1t}	N_1C_{2c}
TZVP/MP2	1.6958	1.3796	1.3811	1.4683	1.4637	1.4639
TZVP/MP2	N_2C_{2t}	$C_{1c}H_{ip}$	$C_{1c}H_{oop}$	$C_{2c}H_{ip}$	$C_{2c}H_{oop}$	
TZVP/MP2	1.4600	1.0893	1.0897	1.0826	1.0934	
TZVP/MP2	$C_{1t}H_{ip}$	$C_{1t}H_{oop}$	$C_{2t}H_{ip}$	$C_{2t}H_{oop}$		
TZVP/MP2	1.0747	1.0931	1.0923	1.0861		

Angles (°)

Method	SCN	NCN	CNC_t	CNC_c	NCH_{ip}	NCH_{oop}
DZ/SCF	118.04	123.93	130.21	119.96	108.5(ass)	108.5(ass)
TZVP/SCF	118.16	123.67	130.34	120.08	108.5(ass)	108.5(ass)

TZVP/MP2	SCN_1	SCN_2	CN_1C_c	CN_1C_t	CN_2C_c
TZVP/MP2	117.77	120.36	117.12	132.29	120.11
TZVP/MP2	CN_2C_t	N_1CN_2	$N_1C_{1c}H_{ip}$	$N_1C_{1c}H_{oop}$	$N_1C_{1t}H_{ip}$
TZVP/MP2	128.55	121.87	107.55	110.86	113.61
TZVP/MP2	$N_1C_{1t}H_{oop}$	$N_2C_{2c}H_{ip}$	$N_2C_{2c}H_{oop}$	$N_2C_{2t}H_{ip}$	$N_2C_{2t}H_{oop}$
TZVP/MP2	109.51	109.47	109.54	111.86	108.39

O-protonated Urea

Bonds (Å) and Angles (°)

Method	CO	OH	CN_1	CN_2	H_{N_1c}	H_{N_1t}
TZVP/MP2	1.3100	0.9655	1.3231	1.3158	1.0060	1.0066
	H_{N_2c}	H_{N_2t}	OCN_1	OCN_2	COH	CN_1H_c
TZVP/MP2	1.0078	1.0053	122.44	114.75	114.11	121.91
	N_1H_t	CN_2H_c	CN_2H_t	NCN		
TZVP/MP2	121.28	118.78	122.60	122.82		

S-protonated Thiourea

Bonds (Å) and Angles (°)

Method	CS	HS	CN_1	CN_2	N_1H_c	N_1H_t
TZVP/MP2	1.7459	1.3381	1.3230	1.3226	1.0051	1.0085
	N_2H_c	N_2H_t	SCN_1	SCN_2	HSC	CN_1H_c
TZVP/MP2	1.0070	1.0077	122.88	116.58	95.49	121.88
	CN_1H_t	CN_2H_c	CN_2H_t			
TZVP/MP2	121.45	121.10	121.98	120.54		

[a] Bond Lengths/Å Bond Angles/°.

[b] H_c is cis and H_t is trans to O or S atom; H_{ip} and H_{oop} are H atoms in the heavy atom planar system and out-of-plane, respectively.

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keep the data small, we give details in full for only the smallest cases, taking just the major contributors for the larger cases.

In much of our previous ^{14}N work [12, 23] 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. The ^{14}N correlation constant for the DZ and TZVP bases were 3.5244 (15.00 mb) [24] and 4.0111 MHz/a.u. (17.07 mb). The best current values for Q_N 20.1 mb (4.7227 MHz/a.u.), Q_H 2.860 mb, Q_O −25.58 mb and Q_S −67.8 mb[24] (1 barn = 10^{-28} m^2 = 100 fm^2) were used for the present studies.

Table 2. Energies (a. u.), Charge distributions (e) and Dipole Moments (D).

$HCONH_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energies	–168.88731	–168.99702	–169.56126		
Mulliken populations	total	total	total	p_π	d_π
O	8.418	8.424	8.299	1.3940	0.0019
C	5.725	5.820	5.820	0.8000	0.0457
N	7.772	7.558	7.494	1.7236	0.0104
H(C)	0.843	0.934	0.934	0.0029	
H_c(N)	0.613	0.723	0.723	0.0099	
H_t(N)	0.629	0.731	0.731	0.0107	
Dipole moment	4.725	4.220^b	3.912		
Stark effect^a	3.714(6)				
Direction from CN bond axis (°)	40.0	40.0	41.5		
Stark effect^a	39.6				

$HCSNH_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energies	–491.51267	–491.62707	–492.15886		
Mulliken populations	total	total	total	p_π	d_π
S	16.075	16.275	16.167	3.357	0.037
C	6.241	5.979	6.086	0.900	0.032
N	7.670	7.473	7.427	1.655	0.011
H(C)	0.782	0.844	0.857	0.003	
H_c(N)	0.608	0.709	0.730	0.009	
H_t(N)	0.624	0.722	0.734	0.010	
Dipole moment	5.285	5.067^d	4.220		
Stark effect^c	4.01(3)				
Direction from CN bond axis (°)	37.5	40.0	39.5		
Stark effect^d	37.5				

HCONHMe

	DZ/SCF	TZVP/MP2		
Total energy	–207.90070	–208.76610		
Mulliken populations	total	total	p_π	d_π
O	8.440	8.311	1.407	0.012
C	5.732	5.834	0.820	0.046
N	7.573	7.372	1.670	0.014
H(C)	0.843	0.928	0.004	
H_t(N)	0.635	0.737	0.009	
C(N)	6.369	6.255	1.110	0.029
H(C_{ip})	0.833	0.870	0.004	
H(C_{oop})	0.788	0.870	0.009	
Dipole moments	4.787	4.017		
Direction from CN bond axis (°)	38.7	33.5		
Dielectric Constant (gas)^e	3.82			

$HCONMe_2$

	DZ/SCF	TZVP/MP2		
Total energy	–246.91230	–247.97149		
Mulliken populations	total	total	p_π	d_π
O	8.452	8.311	1.416	0.012
C	5.736	5.846	0.840	0.046
N	7.355	7.217	1.604	0.017
H(C)	0.852	0.936	0.003	
C_t(N)	6.386	6.273	1.089	0.031
C_c(N)	6.388	6.289	1.124	0.029
H_{ip}(C_t)	0.823	0.865	0.004	
H_{oop}(C_t)	0.804	0.858		
H_{ip}(C_c)	0.830	0.863	0.004	
H_{oop}(C_c)	0.786	0.842		
Dipole moments	4.998	4.192		
Direction from CN bond axis (°)	38.0	34.0		
Dielectric Constant (gas)^e	3.80			

CH_3CONH_2

	TZVP/SCF	TZVP/MP2		
Total energies	–208.05382	–208.78228		
Mulliken populations	total	total	p_π	d_π
O	8.425	8.301	1.405	0.012
C(O)	5.603	5.744	0.788	0.051
C(C)	6.397	6.429		
N	7.566	7.518	1.737	0.010
H_c(N)	0.710	0.726	0.010	
H_t(N)	0.727	0.734	0.011	
Mulliken populations	π_1	π_2	π_3	
O	0.006	0.055	0.648	
C(O)	0.076	0.198	0.121	
C(C)	0.517	0.520	0.000	
N	0.046	0.623	0.206	
H_{oop}(C)	0.353	0.066	0.000	
Total Dipole moment	4.194	3.835		
Stark effect^a		3.678(3)		
Direction from CO bond axis (°)		11.5		
Stark effect^a	10			

CH_3CSNH_2

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energies	–530.54522	–530.68145	–53137912		
Mulliken populations	total	total	total	p_π	d_π
S	16.109	16.301	16.190	1.405	0.012
C(S)	5.994	5.886	5.972	0.788	0.051
C(C)	6.542	6.320	6.382		
N	7.732	7.487	7.444	1.737	0.010
H_c(N)	0.609	0.708	0.728	0.010	
H_t(N)	0.626	0.726	0.738	0.011	

Mulliken populations	π_1	π_2	π_3	
S	1.000	0.000	0.139	0.571
C(S)	0.000	0.036	0.340	0.081
C(C)	0.000	0.563	0.008	-0.007
N	0.000	0.000	0.488	0.347
H_{oop}(C)	0.000	0.396	0.021	0.002
Dipole moment	5.470	5.281	4.330	
Dielectric^g		4.80 (dioxane)		
Dielectric^g		4.53 (C_6H_6)		
Direction from CS bond axis (°)		1.5		

$CO(NH_2)_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energy	–223.93290	–224.07191	–224.82554		
Mulliken populations	total	total	total	p_π	d_π
O	8.487	8.485	8.361	1.481	0.012
C	5.381	5.464	5.630	0.803	0.068
N	7.823	7.587	7.543	1.788	0.011
H_c	0.605	0.704	0.718	0.012	
H_t	0.639	0.734	0.743	0.011	

Table 2 (cont).

Mulliken populations	π_1 MP2	π_2 MP2	π_3 MP2	π_1 SCF	π_2 SCF	π_3 SCF
O	0.061	0.000	0.688	0.250	0.000	0.535
C	0.319	0.011	0.097	0.323	0.012	0.028
N	0.307	0.489	0.106	0.212	0.489	0.216
H_c	0.002	0.003	0.001	0.001	0.003	0.001
H_t	0.001	0.003	0.001	0.001	0.003	0.001
Dipole moment	5.279	4.711	4.360			

$CO(NHMe)_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energy	−301.95653	−302.14539	−303.23079		
Mulliken populations	total	total	total	p_π	d_π
O	8.517	8.511	8.388	1.499	0.012
C	5.300	5.432	5.595	0.825	0.069
N	7.644	7.454	7.405	1.748	0.013
H_t	0.657	0.752	0.762	0.011	
$C_c(N)$	6.401	6.216	6.277	1.056	0.031
H_{ip}	0.746	0.825	0.821		
H_{oop}	0.822	0.891	0.872		
Dipole moment	4.802	4.319	4.043		

$CO(NMe_2)_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energy	−379.94613	−380.18996	−381.48815		
Mulliken populations	total	total	total	p_π	d_π
O	8.567	8.519	8.431	1.582	0.005
C	5.249	5.472	5.605	0.704	0.071
N	7.464	7.297	7.178	1.743	0.006
$C_c(N)$	6.414	6.237	6.314		
$H_{ip}(C_c)$	0.722	0.845	0.865		
$H_{oop}(C_c)$	0.832	0.881	0.843		
$C_t(N)$	6.361	6.241	6.326	0.003	
$H_{ip}(C_t)$	0.853	0.863	0.863	0.003	
$H_{oop}(C_t)$	0.807	0.880	0.865		
Dipole Moment	4.800	4.702	4.292		
Dielectric Constant(C_6H_6)[f]	3.50				

$CS(NH_2)_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energy	−546.55798	−546.70046	−547.42117		
Mulliken populations	total	total	total	p_π	d_π
S	16.153	16.383	16.287	3.531	0.040
C	5.898	5.732	5.832	0.865	0.052
N	7.743	7.514	7.481	1.729	0.011
H_c	0.593	0.734	0.747	0.010	
H_t	0.638	0.623	0.714	0.011	
Dipole Moment	6.394	6.236	5.368		
Dielectric Constant[g]	5.07 (dioxane)				

Mulliken populations	π_1	π_2	π_3	π_4
S	1.000	0.102	0.000	0.682
C	0.000	0.389	0.121	0.051
N	0.000	0.253	0.488	0.132
H_c	0.000	0.001	0.003	0.001
H_t	0.000	0.001	0.003	0.001

$CS(NMe_2)_2$

	DZ/SCF	TZVP/SCF	TZVP/MP2		
Total energy	−702.56639	−702.80701	−704.11307		
Mulliken populations	total	total	total	p_π	d_π
S	16.234	16.443	3.715	0.009	
C	5.803	5.694	0.740	0.049	
N	7.379	7.258	1.675	0.007	
C_c	6.392	6.242			
$H_{ip}(C_c)$	0.844	0.005			
$H_{oop}(C_c)$	0.850				
C_t	6.415	6.258			
$H_{ip}(C_t)$	0.812	0.855	0.003		
$H_{oop}(C_t)$	0.797	0.874			
Dipole Moment	6.531	6.294			
Dielectric Constant[f]	4.65 (C_6H_6)				

$HOC(NH_2)_2^{(+)}$

	TZVP/MP2	
Total energy	−225.17015	
Mulliken populations	Total	π-electrons (6.0043 e)
O	8.260	1.778
C	5.499	0.856
N_1	7.475	1.673
N_2	7.439	1.648
$H_c(N_1)$	0.670	0.009
$H_t(N_1)$	0.671	0.009
$H_c(N_2)$	0.656	0.009
$H_t(N_2)$	0.676	0.009
H(O)	0.654	0.013

$HSC(NH_2)_2^{(+)}$

	TZVP/MP2	
Total energy	−547.77176	
Mulliken populations	Total	π-electrons (8.0048 e)
S	15.859	3.811
C	5.705	0.881
N_1	7.443	1.639
N_2	7.436	1.632
$H_c(N_1)$	0.672	0.009
$H_t(N_1)$	0.682	0.009
$H_c(N_2)$	0.666	0.009
$H_t(N_2)$	0.680	0.009
H(S)	0.85761	0.00619

[a] R. J. Kurland and E. B. Wilson, J. Chem. Phys. **27,** 585 (1957).

[b] TZVP with all-valence CI 3.988D (37.5°).

[c] R. Sugisaki, T. Tanaka and E. B. Wilson, J. Molec. Spectrosc. **49,** 241 (1974).

[d] TZVP with all-valence CI 4.825D (39.5°).

[e] R. M. Meighan and R. H. Cole, J. Phys. Chem. **68,** 503 (1964).

[f] H. Lumbroso and D. Bertin, Bull. Soc. Chim. Fr. 1728 (1970).

[g] G. K. Estok and S. P. Good, J. Phys. Chem. **66,** 1372 (1962).

Table 3. Dipole Moment natural orbital components.

a) Nuclear coordinate systems (a. u.)

Formamide[a]			**Thioformamide**[a]		
Coordinates	x	y	Coordinates	x	y
O	2.269	0.436	S	−1.476	−1.512
C	0.000	0.794	C	0.000	1.209
N	−1.780	−1.059	N	2.524	1.527
H(C)	−0.842	2.691	H(C)	−1.016	2.994
$H_c(N)$	−1.228	−2.875	$H_c(N)$	3.656	0.000
$H_t(N)$	−3.627	−0.649	$H_t(N)$	3.306	3.255

Table 3 (cont).

b) Total dipole moment operator expectation values (a. u.)[b]

Formamide			**Thioformamide**		
Coordinates	x	y	Coordinates	x	y
nuclear	–3.004	–0.438	nuclear	3.069	3.227
electron	1.485	0.192	electron	–1.849	–2.102
total (a. u.)	–1.519	–0.246	total (a. u.)	1.221	1.126
total (D)	–3.862	–0.625	total (D)	3.102	2.861
Total ($\langle r \rangle$)(D)	–3.912		Total ($\langle r \rangle$)(D)	–4.220[b]	

c) Natural orbital composition and Dipole Moment contributions

Formamide			**Dipole Moment Component**	
SCF-MO	Energy (a. u.)	Occupancy (e)	x	y
$1(O_{1s})$	–20.53	1.9996	–2.143	–0.418
$2(N_{1s})$	–15.60	1.9995	1.905	1.077
$3(C_{1s})$	–11.36	1.9993	0.125	–0.775
$4(O_{2s})$	–1.39	1.9863	–1.093	–0.319
$5(N_{2s})$	–1.22	1.9830	0.932	0.596
$6(C_{2s})$	–0.86	1.9751	0.387	–1.217
7	–0.75	1.9694	1.020	0.426
8	–0.68	1.9672	0.603	0.897
$9(\pi)$	–0.61	1.9657	1.188	0.494
10	–0.57	1.9635	–0.911	–0.420
11	–0.44	1.9595	–0.296	–0.089
$12(\pi)$	–0.42	1.9434	–0.989	–0.153
$13(\pi^*)$	+0.13	0.0538	–0.468	–0.357
14	+0.16	0.0307	–0.456	–0.123
15	+0.17	0.0279	–0.994	–0.731
16	–0.20	0.0194	1.257	–0.197
17	+0.27	0.0187	1.854	1.456
18	+0.30	0.0158	2.058	0.895
$19(\pi^*)$	+0.30	0.0156	1.531	0.957

d) Natural orbital composition and Dipole Moment contributions

Thioformamide			**Dipole Moment Component**	
SCF-MO	Energy (a. u.)	Occupancy (e)	x	y
$1(S_{1s})$	–91.91	1.9999	1.380	1.411
$2(N_{1s})$	–15.62	1.9995	–2.619	–1.628
$3(C_{1s})$	–11.35	1.9993	–0.095	–1.307
$4(S_{2s})$	–8.91	1.9994	1.430	1.486
$5(S_{2p})$	–6.59	1.9993	1.371	1.413
$6(S_{2p\pi})$	–6.59	1.9993	1.380	1.411
$7(S_{2p})$	–6.59	1.9992	1.335	1.328
8	–1.27	1.9851	–0.505	–0.503
9	–1.01	1.9815	–0.821	–0.454
10	–0.83	1.9731	–0.085	–1.764
11	–0.76	1.9679	–2.572	–1.746
12	–0.66	1.9632	–1.180	–0.873
$13(\pi)$	–0.54	1.9623	–1.378	–1.250
14	–0.52	1.9602	0.605	0.732
15	–0.34	1.9521	0.767	0.485
$16(\pi)$	–0.33	1.9429	0.062	0.213
$17(\pi^*)$	+0.10	0.0517	0.003	–0.233
18	+0.12	0.0326	0.749	0.551
19	+0.16	0.0269	–0.286	–0.614
20	+0.19	0.0195	–2.908	–1.314
21	+0.24	0.0183	–1.793	–2.053
22	+0.30	0.0162	–1.366	–1.611
$23(\pi^*)$	+0.30	0.0140	–1.953	–1.046
π-electron sum			+0.401	+0.667

Table 3 (cont).

e) All-electron and π-electron dipole moment contributions

Methylformamide			**Dimethylformamide**		
	x	y		x	y
nuclear	–3.098	3.223	nuclear	–1.339	6.224
electron	2.779	–1.675	electron	1.360	–4.574
total	–0.319	1.548	total	0.022	1.649
π-electron	2.916			–0.097	
total (debye)	–0.810	3.934	total (debye)	0.055	4.192
π-MO's Density	x	y	Density	x	y
$1.9707\pi_1$	5.210	–1.075	$1.97\pi_1$	1.704	–3.693
$1.9636\pi_2$	–0.495	–1.220	$1.969\pi_2$	2.152	–3.833
$1.9420\pi_3$	–1.789	2.190	$1.963\pi_3$	–0.521	0.673
$0.0546\pi_4^*$	–0.067	0.039	$1.940\pi_4$	–0.614	3.574
$0.0187\pi_5^*$	0.033	–0.012	$0.056\pi_5^*$	–1.427	3.245
$0.0132\pi_6^*$	0.014	–0.013	$0.020\pi_6^*$	0.014	–0.027
$0.0083\pi_7^*$	0.010	–0.005	$0.017\pi_7^*$	0.022	–0.038
total π_1-π_7^*	2.916	–0.097	total π_1-π_7^*	1.331	–0.099

f) All-electron and π-electron dipole moment contributions

Urea		**Thiourea**	
	z		z
nuclear	–3.376	nuclear	–5.074
electron	1.661	electron	2.962
total	–1.715	total	–2.112
total (debye)	–4.360	total(debye)	–5.376
π-MO's Density	z	Density	z
1.9694 ($1b_1$)	1.086	1.9993 ($1b_1$)	–4.859
1.9604 ($1a_2$)	2.396	1.9671 ($2b_1$)	2.221
1.9496 ($2b_1$)	–2.827	1.9568 ($1a_2$)	4.072
0.0513 ($3b_1^*$)	–0.032	1.952 ($3b_1$)	–2.070
0.0165 ($4b_1^*$)	0.011	0.048 ($4b_1^*$)	0.009
0.0162 ($2a_2^*$)	0.020	0.016 ($2a_2^*$)	0.028
0.0069 ($5b_1^*$)	0.002	0.014 ($5b_1^*$)	0.016
total $1b_1$-$5b_1^*$	0.659	total $1b_1$-$5b_1^*$	0.582

[a] TZVP basis with all-electron correlation by MP2.

[b] The coordinate system is reversed between the formamide and thioformamide molecules. Sign reversed to bring dipole moment sense to same as formamide.

Table 4. EFG (a. u.) and derived NQCC (MHz) at ^{14}N, ^{17}O, ^{33}S and ^{2}H.

$HCONH_2$					
Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+1.114(π)	–0.623(R)	–0.491(T)	0.119
N	TZVP/SCF	+0.954(π)	–0.485(R)	–0.470(T)	0.016
N	TZVP/MP2	+0.876(π)	–0.452(R)	–0.424(T)	0.031
O	DZ/SCF	+2.119(T)	–1.199(R)	–0.921(π)	0.131
O	TZVP/SCF	+1.684(T)	–0.991(R)	–0.693(π)	0.177
O	TZVP/MP2	+1.525(T)	–0.841(R)	–0.684(π)	0.103
H(C)	DZ/SCF	–0.340(R)	+0.175(π)	+0.165(T)	0.030
H(C)	TZVP/SCF	–0.295(R)	+0.153(π)	+0.143(T)	0.034
H(C)	TZVP/MP2	–0.285(R)	+0.151(π)	+0.134(T)	0.059
H_c(N)	DZ/SCF	–0.489(R)	+0.283(π)	+0.206(T)	0.159
H_c(N)	TZVP/SCF	–0.457(R)	+0.271(π)	+0.186(T)	0.187
H_c(N)	TZVP/MP2	–0.426(R)	+0.250(π)	+0.176(T)	0.175
H_t(N)	DZ/SCF	–0.490(R)	+0.287(π)	+0.203(T)	0.172
H_t(N)	TZVP/SCF	–0.465(R)	+0.280(π)	+0.185(T)	0.204
H_t(N)	TZVP/MP2	–0.433(R)	+0.258(π)	+0.175(T)	0.191

Table 4 (cont).

Centre NQCC[b]	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF[a]	-3.926(π)	+2.196(R)	+1.730(T)	0.119
N	DZ/SCF	-5.260(π)	+2.942(R)	+2.352(T)	0.119
N	TZVP/SCF	-4.506(π)	+2.288(R)	+2.218(T)	0.016
N	TZVP/MP2	-4.136(π)	+2.133(R)	+2.003(T)	0.031
N	MWave[c]	-3.848(π)	+1.960(*aa*)	+1.888(*bb*)	0.019
N	MWave[d]	-3.852(π)	+1.980(*aa*)	+1.872(*bb*)	0.028
O	TZVP/MP2	+9.166	-5.055	-4.111	0.103

$HCSNH_2$

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+0.960(π)	-0.572(R)	-0.388(T)	0.192
N	TZVP/SCF	+0.808(π)	-0.434(R)	-0.374(T)	0.074
N	TZVP/MP2	+0.790(π)	-0.425(R)	-0.365(T)	0.076
S	DZ/SCF	+2.528(T)	-2.280(R)	-0.248(π)	0.804
S	TZVP/SCF	+2.168(T)	-1.748(R)	-0.421(π)	0.612
S	TZVP/MP2	+2.182(T)	-1.404(R)	-0.778(π)	0.287
H(C)	DZ/SCF	-0.356(R)	+0.179(π)	+0.171(T)	0.023
H(C)	TZVP/SCF	-0.316(R)	+0.162(π)	+0.154(T)	0.024
H(C)	TZVP/MP2	-0.307(R)	+0.163(π)	+0.144(T)	0.059
H_c(N)	DZ/SCF	-0.450(R)	+0.277(π)	+0.203(T)	0.153
H_c(N)	TZVP/SCF	-0.449(R)	+0.264(π)	+0.185(T)	0.177
H_c(N)	TZVP/MP2	-0.416(R)	+0.243(π)	+0.173(T)	0.169
H_t(N)	DZ/SCF	-0.483(R)	+0.281(π)	+0.203(T)	0.161
H_t(N)	TZVP/SCF	-0.453(R)	+0.270(π)	+0.182(T)	0.194
H_t(N)	TZVP/MP2	-0.425(R)	+0.251(π)	+0.174(T)	0.182

Centre NQCC[b]	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF[a]	-3.383(π)	+2.016(R)	+1.366(T)	0.192
N	DZ/SCF	-4.533(π)	+2.701(R)	+1.831(T)	0.192
N	TZVP/SCF	-3.817(π)	+2.050(R)	+1.767(T)	0.074
N	TZVP/MP2	-3.729(π)	+2.007(R)	+1.723(T)	0.076
N	MWave[e]	-4.2(6)(π)	+2.9(12)(*aa*)	+1.2(6)(*bb*)	0.405
S	TZVP/MP2	-34.186	+22.366	+12.394	0.287
H(C)	TZVP/MP2	-0.206(R)	+0.109(π)	+0.097(T)	0.059
H_c(N)	TZVP/MP2	-0.280(R)	+0.164(π)	+0.116(T)	0.169
H_t(N)	TZVP/MP2	-0.286(R)	+0.169(π)	+0.117(T)	0.182
H(N)[f]	NQR(77K)	0.196(R)	0.114(π)	0.0815(T)	0.168

HCONHMe

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	TZVP/MP2	+0.885	-0.499	-0.386	0.127
O	TZVP/MP2	+1.518	-0.816	-0.702	0.074
H(N)	TZVP/MP2	-0.427	+0.256	+0.171	0.200

Centre NQCC	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	TZVP/MP2	-4.180	+2.356	+1.824	0.127
O	TZVP/MP2	+9.125	-4.902	-4.224	0.074
H(N)	TZVP/MP2	+0.287	-0.172	-0.115	0.074

$HCONMe_2$

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	TZVP/MP2	+0.913	-0.540	-0.372	0.183
O	TZVP/MP2	+1.491	-0.762	-0.729	0.022

Centre NQCC	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	TZVP/MP2	-4.311	+2.549	+1.759	0.183
O	TZVP/MP2	+8.963	-4.582	-4.381	0.022

Table 4 (cont).

CH_3CONH_2

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+1.121(π)	-0.638(R)	-0.483(T)	0.138
N	TZVP/MP2	+0.887(π)	-0.466(R)	-0.421(T)	0.051
O	DZ/SCF	+2.064(T)	-1.301(R)	-0.762(π)	0.261
O	TZVP/SCF	+1.524(T)	-0.774(π)	-0.750(R)	0.016

Centre NQCC[b]	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	-5.293(π)	+3.011(R)	+2.282(T)	0.138
N	TZVP/MP2	-4.190(π)	+2.201(R)	+1.988(T)	0.051
N	DZ/lattice	-2.899(π)	+2.085(R)	+0.814(T)	0.439
N	NQR[f]	(-)2.469	1.741	0.725	0.412

CH_3CSNH_2

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+0.960(π)	-0.587(R)	-0.373(T)	0.223
N	TZVP/MP2	+0.788(π)	-0.443(R)	-0.345(T)	0.125
S	DZ/SCF	-2.538(T)	+2.434(R)	+0.104(π)	0.918
S	TZVP/MP2	+2.118(T)	-1.552(R)	-0.566(π)	0.465
H_c	DZ/SCF	-0.478(R)	+0.276(π)	+0.202(T)	0.155
H_c	TZVP/MP2	-0.417(R)	+0.244(π)	+0.173(T)	0.169
H_t	DZ/SCF	-0.485(R)	+0.282(π)	+0.203(T)	0.162
H_t	TZVP/MP2	-0.426(R)	+0.253(π)	+0.173(T)	0.188

Centre NQCC[b]	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	-4.534(π)	+2.773(R)	+1.761(T)	0.223
N	TZVP/MP2	-3.722(π)	+2.093(R)	+1.629(T)	0.125
N	NQR[f]	(-)1.922	1.399	0.523	0.456
H_c	TZVP/MP2	-0.280(R)	+0.164(π)	+0.117(T)	0.169
H_t	TZVP/MP2	-0.286(R)	+0.170(π)	+0.116(T)	0.162
H	NQR[f]	0.2027	0.1145	0.0882	0.13
H	NQR[f]	0.1937	0.1143	0.0794	0.18

$CO(NH_2)_2$

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+1.261	-0.741	-0.520	0.175
	TZVP/SCF	+1.104	-0.599	-0.506	0.084
	TZVP/MP2	+1.051	-0.581	-0.470	0.105
O	DZ/SCF	+1.862	-1.561	-0.301	0.677
	TZVP/SCF	+1.467	-0.980	-0.487	0.336
	TZVP/MP2	+1.325	-0.925	-0.400	0.396
H_c	TZVP/MP2	-0.437	+0.261	+0.176	0.195
H_t	TZVP/MP2	-0.443	+0.269	+0.174	0.213

Centre NQCC	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	TZVP/MP2	-4.966	+2.745	+2.221	0.105
O	TZVP/MP2	+7.965	-5.559	-2.406	0.396
H_c	TZVP/MP2	-0.293	+0.175	+0.118	0.195
H_t	TZVP/MP2	-0.297	+0.180	+0.117	0.213

$CO(NHMe)_2$

Centre EFG	Basis	q_{zz}	q_{yy}	q_{xx}	η
N	DZ/SCF	+1.347(π)	-0.750(R)	-0.597(T)	0.114
	TZVP/MP2	+1.119(π)	-0.576(R)	-0.543(T)	0.030
O	DZ/SCF	+1.821(T)	-1.570(R)	-0.250π)	0.725
	TZVP/MP2	+1.288(T)	-0.942(R)	-0.346π)	0.463

Table 4 (cont).

Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
NQCC					
O	TZVP/MP2	+7.744	–5.665	–2.079	0.463
N	TZVP/MP2	–5.283	+2.720	+2.562	0.030
N	NQR[g]	(–)4.0344	(+)2.6661	(+)1.3683	0.3217
$CO(NMe_2)_2$					
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
EFG					
N	DZ/SCF	+1.400(π)	–0.827(R)	–0.573(T)	0.181
	TZVP/SCF	+1.255(π)	–0.661(R)	–0.594(T)	0.054
O	DZ/SCF	+1.877(T)	–1.677(R)	–0.200π)	0.787
	TZVP/SCF	+1.542(T)	–1.088(R)	–0.454π)	0.411
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
NQCC					
N	TZVP/SCF	–5.926	+3.121	+2.805	0.054
N	NQR[g]	(–)4.887	(+)2.505	(+)2.382	0.0025
$CS(NH_2)_2$					
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
EFG					
N	DZ/SCF	+1.154(π)	–0.716(R)	–0.438(T)	0.175
	TZVP/SCF	+0.999(π)	–0.584(R)	–0.415(T)	0.169
	TZVP/MP2	+0.978(π)	–0.573(R)	–0.406(T)	0.171
S	DZ/SCF	–3.103(R)	+2.260(T)	+0.842(π)	0.457
	TZVP/SCF	–2.475(R)	+1.911(T)	+0.564(π)	0.544
	TZVP/MP2	–2.027(R)	+1.865(T)	+0.162(π)	0.840
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
NQCC					
N	TZVP/MP2	–4.621	+2.705	+1.916	0.171
S	TZVP/MP2	–32.285	+29.702	+2.583	0.840
$CS(NMe_2)_2$					
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
EFG					
N	DZ/SCF	+1.232(π)	–0.742(R)	–0.490(T)	0.204
N	TZVP/SCF	+1.087(π)	–0.621(R)	–0.466(T)	0.142
Centre	Basis	q_{zz}	q_{yy}	q_{xx}	η
NQCC					
S	DZ/SCF	–3.354(R)	+2.451(T)	+0.903(π)	0.462
S	TZVP/SCF	–2.709(R)	+2.167(T)	+0.541(π)	0.600

[a] Scaled for best least–squares fit (see Text); DZ/SCF 3.525 MHz/a. u and TZVP/SCF 4.0111 MHz/a. u.

[b] Using q_N 20.1 mb(4.723 MHz/a. u.)

[b] (for other nuclei see Text).

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2. Results

2.1. The Equilibrium structures and a comparison with microwave and other experimental structures

The structures (Table 1) of both formamide and thioformamide are close to the MW substitution structures [4, 25, 26]. The MW spectrum of acetamide and other related compounds is complex owing to the coupling of Me torsion with NH_2 inversion [27 - 29] but all of these amides have planar skeletons. The twisted form (NH_2 group perpendicular to the OCN plane) is a transition state [30], and our own studies confirm this. The neutron diffraction structure for acetamide at –165°C, and the electron diffraction structures are close to the present structure, with the single exception of the CN bond, where the lengths are different by –0.029 and +0.014 Å, respectively. Although structures for methyl- and dimethyl-formamides have been reported from x-ray diffraction of the liquid phases, the results are insufficiently well determined to be compared with the present work [31 - 33]. In these studies, the HN and CO are *trans* in methylformamide [32]. A number of clathrate compounds with formamide and DMF solvation have been reported by x-ray crystallography, but it seems these are inappropriate for comparison with the present study. A wide series of 4-21G equilibrium structures has been reported [34] which contains amides, but little detail is given. In view of the probable steric hindrance, the calculations on both tetramethyl-urea and -thiourea were started with non-planar structures of C_1 symmetry; however, in both cases the out of plane torsion angles reduced to near zero, and lower energy minima were found with the planar structures, but with substantial CNC angle distortions and shortening of the CH bonds with closest H, H appoach. In both cases, the 'gear-wheel' conformation was chosen, such that one H was staggered with respect to those on the sterically closest approach. Two conformations are possible, with C_S and C_1 symmetry. The two conformations differ in energy by 2.700 kJmol^{-1}, with the C_S symmetry conformer being the lower in total energy. This is similar to many other CH_3 rotation barriers.

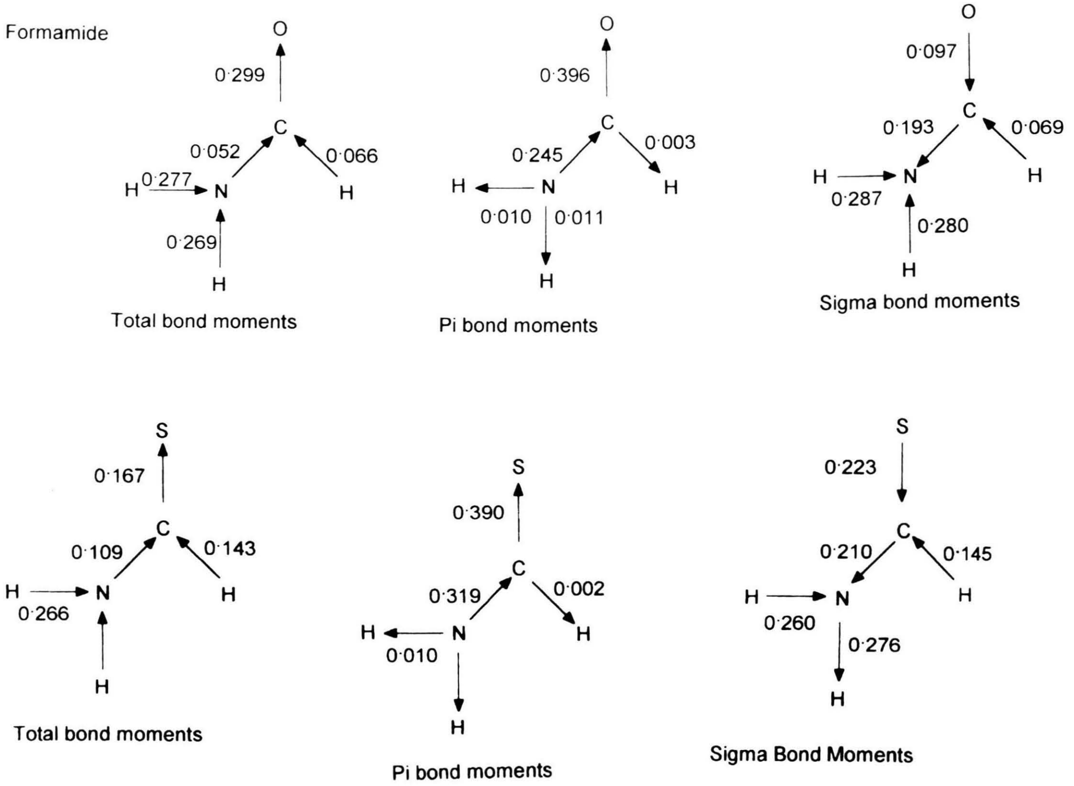

Fig. 1. a), b) Total, π-bond and σ-bond moments for formamide and thioformamide.

2.1.2. The protonated forms of urea and thiourea

Compared with the neutral molecules, urea and thiourea, being O- and S-protonated, which is the stable form in each case, show the expected change of C=O and C=S bonds towards C–O and C–S, respectively, with a lengthening of 0.09 and 0.08 Å, respectively, with corresponding shortening of the CN bonds by about 0.05 and 0.03 Å, respectively, and slight inequalitities in the CN bonds through the reduction in symmetry from C_{2v} to C_S.

2.2. Charge distribution in simple amides and thioamides

2.2.1. Mulliken Charge Distributions

In connection with ionisation processes [35, 36], the claim has been made that the charge in amides and thioamides favours N over O, and S over N, respectively. Using the Mulliken analysis data from Table 2, we convert the set of charges, by summation around centres, into a set of 'bond dipoles', as reported previously [38 ,39], either as total contributions or by partitioning the populations in π- and σ-orbitals separately. For brevity only the TZVP/MP2 results are shown; the SCF results are similar, but with larger dipoles on almost all bonds. The more illuminating set are the separate π- and σ-bond dipoles, and typical examples are shown in Figs. 1a to 1e. For example, with formamide (Fig. 1a), the total bond dipoles show a drift of electrons, relative to the neutral atoms, from H to both C and N, and from N to C and O; however, the separate π-bond dipoles are much larger than the total values, showing that the σ-sets are polarised from O towards C and N, with the σ-CO bond polarisation near 0.10 e, and σ-CN polarisation near 0.20 e. The π contributions are in the reverse direction and near 0.40 e and 0.25 e, respectively. In the following section the order of bonded atoms AB are in the sense δ+ and δ-, respectively. Minor non-integral numbers of π-electrons, arising from the MP2 method, are responsible for incomplete charge balances. These do

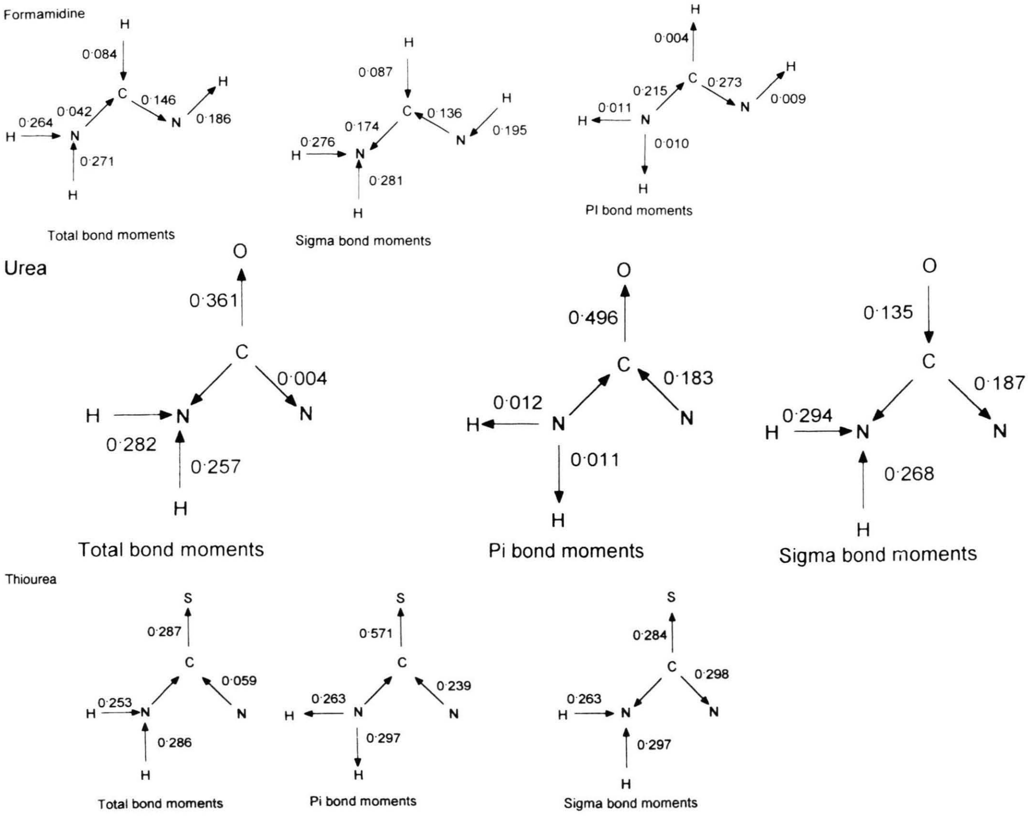

Fig. 1. c), d), e) Total, π-bond and σ-bond moments for formamidine, urea and thiourea.

not affect the conclusions, which relate to large shifts.

Thioformamide (Fig. 1b) is similar in total bond dipoles to the O analog; the CS bond is polarised towards S by about 0.17 e, the NC bond towards C by about 0.11 e, with the HC/HN bonds as previously. However, the π-electrons lead to bond dipoles on the CS bond of 0.39 e towards S, and the NC bond polarised towards C by 0.32 e. The σ-components show a large polarisation of CS (0.22 e), with the negative end at C, with CN also polarised towards N by about 0.21 e. Thus the Mulliken bond dipoles clearly indicate the reason for the difference of the O and S series of dipole moments: the σ-bond is much more strongly polarised in $CSNH_2$ than in $CONH_2$, towards C from S and O, respectively.

The situation with the other molecules is similar to the above, and we choose cases where there are two NH_2 groups. In urea (Fig. 1d and 4) the π-system is polarised towards O from N via C, with NC and CO bond dipoles of 0.18 and 0.49 e, respectively. The σ-system has the reverse polarisation from O via C towards N, with components OC 0.13 and CN 0.19 e respectively. The thiourea (Fig. 1e and 5) π-system has N via C to S polarisation with bond dipoles of 0.24 e (NC) and 0.28e(CS), while the σ-system has the S via C to N polarisation, with bond dipoles SC 0.27 e and CN 0.18 e, respectively.

It is clear that the enhanced transfer of electrons from N via C to S over N via C to O in the π-system can be regarded as an enhanced resonance effect, as discussed previously. However, the effect is probably a "push-pull" mechanism; relative to C, N is a very strong σ-acceptor, and S is a better σ-donor than O, enabling the back-donation from N in the π-system to be enhanced in the S case. These effects are not based upon electronegativity alone however, since when formamidine is treated in a similar manner (Table 1c and 6), the fact that the central C atom is now bonded to two N atoms, still leads to the σ-bonding being polarised in the direction NH via C to NH_2, with the π-bonding polarised in the reverse direction. Hence the effect seems to arise from the differential contribution of 2π-electron from the CO, CS and CNH groups, but 2π-electrons from the N atom. Similar effects are apparent in our studies of esters and dithioesters, to be published later.

The O-protonated form of urea shows a loss of about 0.1 -0.15e from O, C and N, with the remainder being lost from the H-atoms; in thiourea the loss of density on the S atom is larger (0.4 e), but with similar changes at C, N and H to those for urea. However, the π-density at O and S is larger in the protonated case than in the neutral one by nearly 0.3 e, showing that almost all the overall loss at these atoms is by additional σ-bond polarisation. These all reflect the increase in delocalisation produced by addition of a proton, the CN/CO bond lengths changing toawards a more even set, with parallel changes in thiourea.

2.2.2. Dipole Moments; some general comments

In order to analyse the individual MO or natural orbital(NO) contributions to the overall dipole moment (or EFG tensor element), we must be aware of the nuclear terms, which depend upon the coordinate system used in the calculation. Here we use the 'centre of nuclear charge' system, in which the orientation of the molecule is chosen such that the origin is the centre of nuclear charge. It will be seen below that the average position of some core electrons is effectively the same as the coordinates of the atom concerned, but with a change of sign. The *sum* of the nuclear and electron terms defines the dipole moment. In Table 3, we give both the NO contribution to the wave-function (in electrons), restricting to the largest terms, and the total contribution of that NO to the overall DM. The separate π-electron components are also given. The dipole moment component shown is for a total occupancy of 1-electron; hence the actual contribution to the dipole moment is the product of these x,y-figures with the NO occupancy. Examples with dipole moment and EFG tensor elements are shown in Figs. 2 to 6.

The π-MO's and NO's, which form an important part of the present discussion, are basically heteroatom substituted versions of the allyl anion (in the case of the amides and thioamides) and the trimethylenemethane dianion (for the ureas and thioureas); thus the Hückel picture of the allyl anion has a bonded MO (π_1, $1b_1$) covering all centres, with no out of plane nodes, and a non-bonded (π_2) MO with the centre atom nodal ($1a_2$). These simple methods can be mapped onto the present methodology. We take the more general case of acetamide and thioacetamide in the present results. The acetamide π-NO's (Table 3) show that π_1 has most of the total population in the CH_3 group, π_2 on the N atom (and no nodes perpendicular to the molecular plane), while π_3 is nodal between C and N, with populations mainly on the O-atom; residues lie in the CH_3 group. Thioacetamide has π_1 localised 99% on S as $2p_\pi$, with π_2 similarly 96% localised in the CH_3 group. π_3 which compares with π_2 in acetamide, is more evenly distributed with S, C(S), and N populations of 14, 34 and 49%. The highest π-NO (π_4 for thioacetamide), has population mainly on the S-atom. Hence the two highest occupied π-orbitals for the pair of molecules behave similarly, being strongly polarised in opposite directions in each molecule. Taken together, the two NO's present a very similar total population pattern for amide and thioamide.

The urea and thiourea π-MO's are similar, and both related to the trimethylenemethane $1a'' + 1e''$ MO's but with the latter split into $1b_1$ and $1a_2$. The C_{2v} structures lead to $1a_2$ and its corresponding NO almost totally localised on N. There are significant changes in the π-MO's and corresponding π-NO's (Table 3), with the nearly 3-fold symmetry of $1b_1$ at the SCF level being strongly mixed with $2b_1$ at the MP2 level.

2.2.3. Total Dipole moments and experimental comparisons

Owing to low vapour pressures, several of the present compounds have been studied in solution rather than MW spectroscopy. Amides and thioamides are known from these measurements to self-associate in benzene, leading to problems with extrapolation of data to infinite dilution; however, dioxane appears not to show this effect. Thus the same authors found values for acetamide of 3.07 D (C_6H_6) and 3.70 D (dioxane) [39]. The gas-phase value for the dipole moment is 3.68(3) D from the Stark effect on the MW spectrum [28] and close to our present MP2 value of 3.84 D. Hence we have some reservations regarding the substituted urea and thiourea values found experimentally. In the following discussion we concentrate upon the calculated MP2 values, unless otherwise mentioned. The results (Table 2) show that the DZ and TZVP bases generally lead to values larger than experiment at the SCF level, but these are reduced to close to experimental values at the MP2 level.

The calculated direction of the moments for both formamide and thioformamide are very close to the

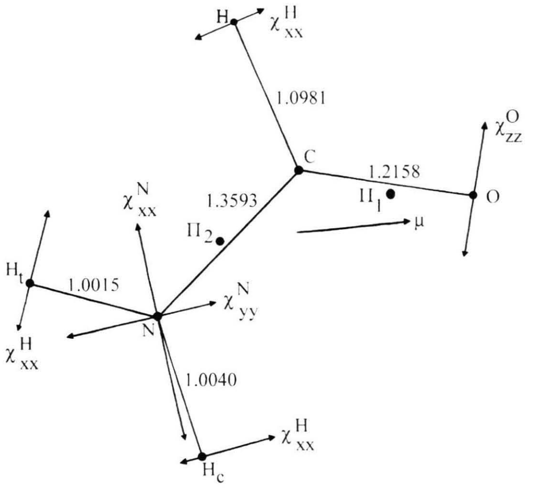

Fig. 2. EFG and average π-electron position from the TZVP/MP2 natural orbital calculations for formamide.

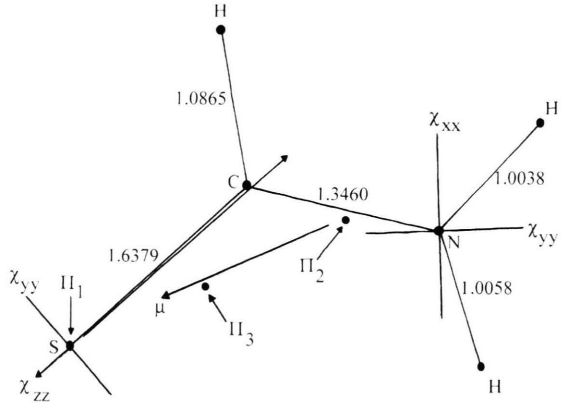

Fig. 3. EFG and average π-electron position from the TZVP/MP2 natural orbital calculations for thioformamide.

MW ones, and both lie close to the line from the midpoint of the $(H_2)NC$ bond and the O or S atom (Figs. 2 and 3), respectively. Similarly the directions for the mono- and di-methylated formamides lie close to the N-O atomic (nonbonded) axis. The electron diffraction structure for acetamide [29], used as a template for the MW analysis, shows that the dipole moment for the molecule lies very close to the CO bond direction; the present work (MP2) finds an angle between the CO bond axis and the dipole moment of about 11.5°, with the tilt towards the CH_3 group. This is consistent with formamide and a CH_3 group replacement of the H atom, since the dipole moment for formamide lies by about 13.5° from the CO bond axis, and towards the H-atom.

The present results on total dipole moments agree with the experimental determinations as to the order formamide < thioformamide, urea < thiourea, tetramethylurea < tetramethylthiourea. There is every reason to think this is likely to be general.

2.2.4. Dipole moment σ- and π-components

Comparison of the nuclear coordinate positions (Table 4a) with the average positions (<er>) of the core and inner valence (e. g. O_{2s}, N_{2s}) electrons, for formamide and thioformamide, shows that these electrons are heavily localised, as expected. The change of sign arises from the electronic charge in <er> and *addition* of the nuclear and electronic components. The dipole moment, unlike the EFG, is invariant to the reference centre, but is conventionally determined at the centre of mass, as here. Formamide has a large μ_x component (the x-axis lies 8° from the CO bond), and small μ_y component; the sum over the first 5 π-NO's yields very small polarisation totals (Table 4), such that almost all of the total electronic components arise from σ-bond polarisation. The value of the operator in (1) for each MO lies in the range ± 3 a. u., and the contribution from the natural orbitals declines quickly, owing to the low NO occupancy. Hence summation of the first few terms is appropriate. Indeed, the average positions of the π-electrons, highly occupied $1a''$ and $2a''$ shown in Fig. 1 indicates that the electrons lie very close to the midpoints of the CO and NC bonds respectively. This confirms the low polarisation of the π-electrons; at the SCF level, the π-electrons are much more delocalised, with the centroids of the $1a''$ and $2a''$ MO's lying near the centroid of the NCO triangle. Thus the π-electrons do not behave as a group from the point of view of delocalisation, since for the allyl anion, which is isoelectronic but homopolar, the centroids of both $1b_1$ and $1a_2$ would be at the central C-atom.

Comparison of thioformamide with formamide at the TZVP/MP2 level (Figs. 2 and 3) shows that the π_1 NO lies very close to the S-atom ($S_{2p\pi}$), π_2 relatively close to the CN midpoint, but slightly off-the bond axis (towards the S side), while π_3 lies well off the internuclear axes, and close to the SN axis (Figure 3). Acetamide and thioacetamide show the same phenomenon; for the S-compound, π_1 (S_{2pp}) lies close to the S atom, $\pi_2(CH_3)$ lies close to C_{Me}, π_3 near the NC bond but closer to C than N, while π_4 lies well off the interbond axes and close to the

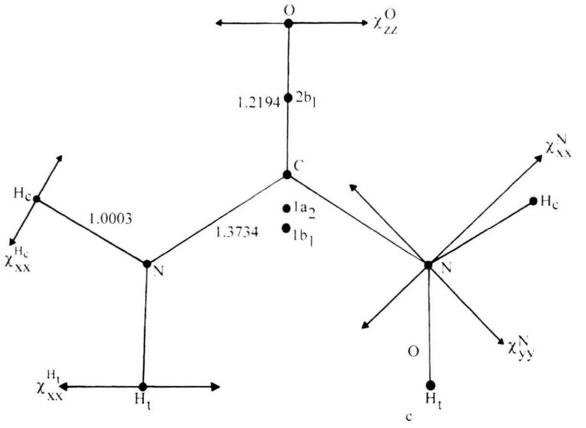

Fig. 4. EFG and average π-electron position from the TZVP/MP2 natural orbital calculations for urea.

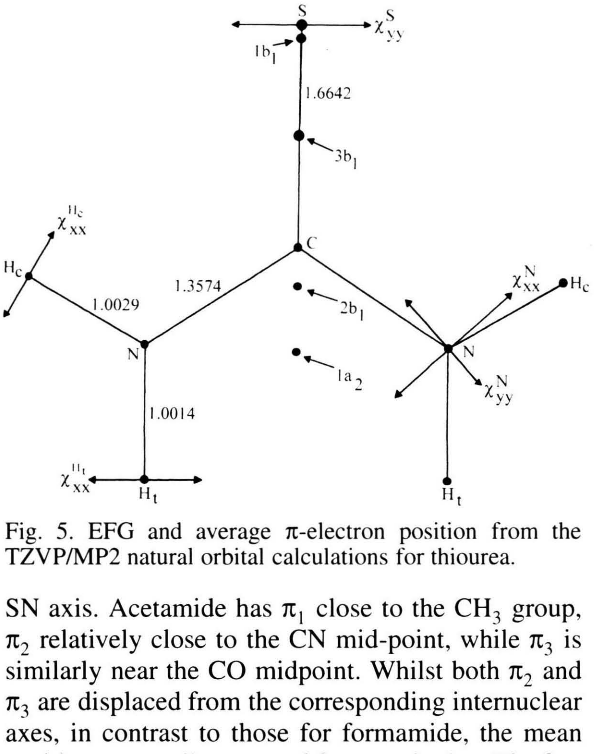

Fig. 5. EFG and average π-electron position from the TZVP/MP2 natural orbital calculations for thiourea.

SN axis. Acetamide has π_1 close to the CH_3 group, π_2 relatively close to the CN mid-point, while π_3 is similarly near the CO midpoint. Whilst both π_2 and π_3 are displaced from the corresponding internuclear axes, in contrast to those for formamide, the mean positions are well-separated from eachother. The fact that π_3 and π_3 in thioformamide and thioacetamide, respectively, lie so far off the bond axes, and relatively close to the SN axis, is a sign of strong delocalisation in these compounds, relative to the O-analogs.

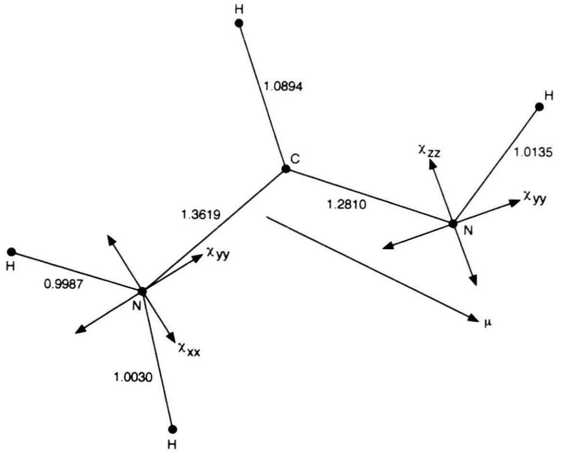

Fig. 6. EFG and average π-electron position from the TZVP/MP2 natural orbital calculations for formamidine.

2.3. Localised molecular orbitals

Since the NO and MO EFG contributions are fully delocalised and do not offer a simple interpretation, we have converted the NO's to localised orbitals (LMO's) [40]. This technique, usually employed with the SCF MO's [41], is useful in cases where the presence or absence of bonds is important; the technique maximises the distance between the centroids of the electron pairs by an orthogonal transformation of the density matrix. In effect, the LMO is a conversion of the delocalised MO's (an $N \times N$ AO by MO matrix) to a set of N off-diagonal terms. The EFGs are then evaluated from the resulting wave-function. A feature of σ/π-systems is that such localisations with the total wave-function in one stage leads to σ+π MO's forming 'banana bond' pairs [42], which by definition have centroids at the same in-plane position, but above and below the plane. This is overcome by separate localisation of the σ- and π-MO's or NO's. Another feature of this transformation is that lone pair MO's on carbonyl groups, which are usually defined by a_1 and b_2 symmetry adapted MO's, mix to form 'rabbit ears' pairs; these are totally equivalent in density terms but unhelpful for spectroscopic purposes. For further discussion of the role LMO's can play in (photoelectron) spectroscopy, see [46].

In the cases shown (Table 5) we have given a set of NO contributions for selected molecules, such as

Table 5. Natural and Localised Orbital contributions to the EFG[a,b,c,d].

5a) Formamide TZVP/MP2

total contributions

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	−0.121	−0.644	0.764	0.344
electron	−0.304	0.192	0.111	−0.344
total	−0.424	−0.452	0.876	0.000

Integrals over natural orbitals

Natural orbital	q_{zz}	q_{yy}	q_{xx}	q_{xy}
1	−0.012	0.024	−0.012	−0.005
2	0.000	0.000	−0.001	−0.000
3	−0.006	0.064	−0.059	−0.081
4	−0.004	0.034	−0.030	−0.017
5	0.021	0.037	−0.058	−0.004
6	0.097	−0.031	−0.066	−0.038
7	−0.150	0.615	−0.465	0.562
8	0.951	−0.456	−0.495	0.064
9(π)	−0.650	−0.632	1.283	−0.017
10	−0.021	0.173	−0.151	−0.199
11	−0.130	0.492	−0.361	−0.432
12(π)	−0.248	−0.223	0.471	−0.006
13(π*)	−0.447	−0.416	0.863	−0.022
14	−0.039	0.359	−0.320	−0.452
15	0.011	0.022	−0.034	−0.033
16	−0.708	1.893	−1.185	−1.163
17	2.836	−0.911	−1.925	2.184
18	−0.235	0.446	−0.212	−0.362
19(π*)	−1.652	−1.645	3.297	−0.003

LMO contributions[d] to the ^{14}N EFG

Localised orbital	q_{zz}	q_{yy}	q_{xx}	q_{xy}
NH$_c$	1.053	−0.528	−0.525	−0.015
NH$_t$	−0.141	0.662	−0.521	0.674
π–NC	−0.876	−0.867	1.744	−0.008
σ–NC	−0.133	0.635	−0.502	−0.657
π–CO	−0.025	0.015	0.010	−0.011

5b) Methyl formamide

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	−0.728	−0.216	0.945	−0.205
electron	0.325	−0.267	−0.058	0.205
total	−0.404	−0.483	0.886	0.000

Individual LMO contributions to the EFG

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
π–CH$_2$	−0.019	0.030	−0.011	0.019
π–CO	0.016	−0.028	0.012	−0.007
σ–NCH$_3$	−0.233	0.724	−0.491	0.565
σ–NH	0.024	0.495	−0.519	−0.747
σ–NC(O)	1.007	−0.500	−0.507	0.152
π–NC(O)	−0.858	−0.879	1.737	0.003

5b) Dimethyl formamide

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	−0.692	−0.428	1.120	0.165
electron	0.331	−0.130	−0.201	−0.165
total	−0.361	−0.555	0.920	0.000

Individual LMO contributions to the EFG

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
π–CH$_3$	−0.008	0.018	−0.011	−0.028
π–CH$_3$	−0.011	0.022	−0.011	0.026
π–CO	0.009	−0.024	0.015	−0.015
σ–NC(O)	1.007	−0.503	−0.504	−0.125
σ–N(CH$_3$)	−0.005	0.499	−0.493	0.700
σ–N(CH$_3$)	−0.195	0.682	−0.486	−0.589
π–NC(O)	−0.856	−0.879	1.735	−0.001

Table 5 (cont).

5d) Urea

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	−0.778	−0.059	0.838	0.256
electron	0.197	−0.399	0.202	−0.256
total	−0.581	−0.459	1.040	0.000

Individual LMO contributions to the EFG

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
NH$_c$	−0.485	1.006	−0.521	−0.245
NH$_t$	0.425	0.090	−0.514	0.756
σ–NC	0.799	−0.308	−0.491	−0.496
π–NC	−0.901	−0.913	1.813	−0.004

5e) Thioformamide

Total Natural Orbital contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	0.058	−0.859	0.801	−0.090
electron	−0.423	0.434	−0.011	0.090
total	−0.365	−0.425	0.790	0.000

Integrals over natural orbitals

Natural orbital	q_{zz}	q_{yy}	q_{xx}	q_{xy}
5	−0.049	0.109	−0.061	0.045
6(π)	−0.006	0.014	−0.008	−0.006
9	0.012	0.039	−0.050	−0.011
10	0.121	−0.011	−0.110	0.128
11	0.968	−0.291	−0.676	−0.752
12	−0.112	0.612	−0.500	0.614
13(π)	−0.551	−0.510	1.061	0.010
14	−0.133	0.268	−0.135	−0.013
15	−0.097	0.211	−0.113	0.049
16π)	−0.338	−0.325	0.663	−0.003

LMO contributions to the ^{14}N EFG

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
π–CS	0.036	−0.003	0.039	0.004
NH$_c$	1.014	−0.485	−0.530	0.276
NH$_t$	0.105	0.418	−0.523	−0.772
σ–NC	−0.332	0.837	−0.505	0.492
π–NC	0.852	−0.833	1.685	0.008

5f) Thiourea

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	−0.873	−0.005	0.877	0.154
electron	0.303	−0.409	0.106	−0.154
total	−0.570	−0.414	0.983	0.000

LMO contributions to the ^{14}N EFG

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
NH$_t$	0.249	0.267	−0.516	0.777
NH$_c$	−0.416	0.942	−0.526	−0.407
σ–NC	0.899	−0.404	−0.495	−0.367
π–NC	−0.874	−0.892	1.766	−0.004

5g) O–protonated urea

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	0.079	−0.957	0.878	0.080
electron	−0.382	0.392	−0.010	−0.080
total	−0.303	−0.565	0.868	0.000

Table 5 (cont).

LMO contributions to the EFG at ^{14}N

LMO	q_{zz}	q_{yy}	q_{xx}	q_{xy}
NH_t	0.759	–0.226	–0.533	–0.631
NH_c	0.572	–0.041	–0.531	0.737
σ–NC	–0.504	1.010	–0.506	–0.104
π–NC	0.885	–0.857	1.742	–0.002

5h) S-protonated thiourea

Total LMO contributions to the EFG at ^{14}N

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
nuclear	0.061	–0.963	0.902	0.063
electron	–0.346	0.430	–0.084	–0.063
total	–0.285	–0.533	0.818	0.000

LMO contributions to the ^{14}N EFG

	q_{zz}	q_{yy}	q_{xx}	q_{xy}
NH_c	0.796	–0.262	–0.534	–0.605
NH_t	0.529	0.002	–0.531	0.754
σ–NC	–0.497	1.004	–0.507	–0.149
π–NC	–0.866	–0.836	1.703	–0.003

[a] TZVP basis with all–electron correlation by MP2.

[b] Coordinate systems as shown in Table 4.

[c] The natural orbital sequence numbers are the same as Table 4.

[d] LMO contributions < 0.05 in χ_{zz} omitted.

formamide and thioformamide, and the nuclear and electronic terms leading to the total tensor elements for all molecules. This is followed by the principal contributors to the EFG; χ_{ii} less than 0.05 are excluded, except π-NO contributions. Small differences occur between the LMO totals in Table 5 and those for NO's in Tables 4 and 5. These arise from truncation of the summation of terms in the LMO to the large (SCF occupied) components only.

2.3.1. LMO for formamide, urea and their methyl derivatives

The LMO positions (Figs. 1 to 6) for these compounds show very constant features as expected. The σ- and π-LMO of the CO bond in formamide and its methylated derivatives have centroids near 0.5 and 0.39 Å from the O atom. The CN σ and π-LMO's are slightly more variable, with a trend on methylation (NH_2, NHMe, NMe_2) of σ-LMO 0.60 to 0.57 Å, and π-LMO 0.16 to 0.22 Å, showing the increase on π-donor capacity. HC(Me), HC(O) and HN bonds are localised about 0.30, 0.34 and 0.43 Å from the H atoms, respectively. The 'rabbits ears' lone pair orbitals are quite strongly removed from the sp^2 hybrid orbital positions; the 2 LP_O orbitals are effectively identical, but with C-O-LP_O angles of about 108 rather than 120° for the hybrid. This is consistent with the much higher p-orbital composition than sp^2. The position with urea is rather similar in most respects, but here the 2 LP_O LMO's make an even less obtuse angle, with both at about 103° from the C-O bond. σ- and π-LMO of the CO bond are about 0.51 and 0.30 Å from the O-atom; the corresponding positions for tetramethylurea are 0.58 and 0.33 Å, with the LP_O making an angle of 105° to the CO axis.

When urea is O-protonated, the HO bond centroid becomes near the OH midbond (0.51 Å from H), with the σ- and π-LMO of the CO bond lying 0.55 and 0.11 Å from the O atom, respectively. Clearly the π-LMO centroid lies closer to the O atom than in the neutral molecule, again consistent with the greater positive charge on the central C atom in the cation. Here the LP_O lies at 118° from the CO bond axis, much closer to the sp^2 value, with the angle HOC at 114°. Although strictly non-equivalent, the 2 N atoms are very similar, the σ- and π-LMO of the CN bonds lying at 0.59 and 0.22 Å from the N atom. Thus the CN and CO bonding shows the greater donating power of N over O. The protonation of urea has been studied by differences in the topology of the charge distribution [44], both from the point of view of the internal H-bonding between molecules, and the direct effect of the H(O)-addition. The results again demonstrate that protonation reduces the π-component of the N EFG, with concurrent increase along the H-N bonds, but beyond this there is no immediate method of relating the two procedures.

2.3.2. LMO for thioformamide, thiourea and their methyl derivatives

The σ- and π-LMO's of the SC bonds are at 0.90 and 0.54 Å from the S atom, so that the centroid of the σ-bond is closer to C than the midpoint. The LP_S LMO's are again nearly equivalent, with distances of 0.52 Å from S and making C-S-LP_S angles of 105°. The σ- and π-LMO of the CN bonds are 0.57 and 0.19 Å from the N atom, both slightly larger than in formamide under the same level of calculation. This is consistent with the slightly higher electron donating effect of N in the thio-compound. The situation with thiourea is similar to both thioformamide and urea; the σ- and π-LMO of the SC bonds are at 0.94 and 0.40 Å from S, with a C-S-LP_S angle of 103°. S-protonation of thiourea gives a structure with HSC angle 105° and the C-S-LP_S angle 128°; The σ- and π-LMO centroids for SC are 0.96 and 0.19 Å from S, again showing quite high π-localisation on S, with the σ-bond centroid closer to C than S.

2.4. Electric Field Gradients and derived NQCC

In previous papers we have discussed the effect of condensation on the NQCC at ^{14}N, in the light of monomer calculations which compare with the gas phase molecules, and cluster or lattice calculations, both of which refer to the condensed phase [11, 12]. The present results include systems such as formamide, acetamide, urea and thiourea, where we have previously discussed the relationship of the Hartree-Fock SCF results to experiment. We do not add to that discussion here except for a few points in relation to the MP2 correlated calculations. First, the magnitude of the EFG at almost all nuclei and almost all molecules is reduced; hence the NQCC are numerically smaller for the MP2 calculations, and the use of the 'best values' for the atomic quadrupole coupling constants (Q_Z) already brings the results into the area for agreement with experimental gas-phase work, without 'scaling' (as was necessary with the DZ-SCF results). In only a few cases, largely restricted to ^{17}O NQCC's, are the individual NQCC's changed in order between the TZVP/SCF and TZVP/MP2 calculations, but the DZ to TZVP change leads to more interchanges in χ_{ii}. Further discussion of the results in Table 4 in relation to NQR studies, where the single molecule calculations have limited applicability, are delayed to a following paper using lattice calculations [45].

2.4.1. The MO, NO and LMO contributions to the EFG

For (x, y) planar molecules, the EFG (3×3) matrix has one off-diagonal element (q_{xy}). The diagonalalised tensor in general has non-zero nuclear and electronic q_{xy} but the sum is zero, and this is shown in Table 5. Normally the values obtained for the individual MO's are based upon a 1-electron occupancy and are then multiplied by the occupation numbers for the MO (2 or 0). Many examples of MO contributions in such cases have been reported previously [46, 47]. When MP2 correlation is employed, the occupancy varies widely but again the NO contribution is the product of the occupancy and orbital contributions. The delocalised NO's, like the starting MO's, show many orbitals making EFG contributions. The LMO's largely remove this tendency, and reduce the main terms to just 3 bonds (or 2 bonds and a lone-pair at O or S). Hence the data in Table 5 is limited to those LMO's, together with the other π-LMO's.

The first thing to emerge from Table 5 is the strong relationship to the Townes-Dailey theory; the LMO contributions show very uneven values for the individual EFG components, as evidenced by the NH bond contributions. This is because of the very differing contributions of the nuclei to the nuclear part, owing to different geometric positions. It is possible to make some general conclusions about the EFG LMO components, especially in the out-of-plane (oop)directions, since these are invariant to rotation of the molecule around the oop-axis. Both in Tables 4 and 5, xx, yy, zz are used strictly according to (1) and do not refer to the molecular coordinate system.

Detailed analysis of the EFG tensor elements from the LMO's (Table 5) shows that the out-of-plane components (π-NC) at ^{14}N, q_{zz} are large and positive, and generally close to +1.7 a. u. for each of the formamides. The three σ-bonded components (σ-NC, NH$_c$ and NH$_t$) are all similar and close to –0.5 a. u. The resultant of the 4 terms (+0.21 a. u.) lies close to the total electronic component but is reduced further by the more distant terms. Together with the positive nuclear components, these lead to the observed negative NQCC at these centres. The contributions to q_{zz} from the NH and NMe groups are all similar. When we compare with urea, the three σ-bonded components are still similar, but π-NC has increased slightly, which with the positive nuclear component leads to a higher (negative) NQCC. A similar comparison of formamide with its thio-derivative again shows that the oop-components are very similar in their effect on χ_{zz}, namely close to –0.5 a. u. for NH and σ-NC, while π-NC is lower at +1.69 a. u.; again not all the electronic component can be accounted for by the 4 LMO terms. The full resultant, with a slightly larger (positive) nuclear component, leads directly to the smaller (negative) NQCC at ^{14}N in the thioamide (Table 4). Finally, the comparison of urea with thiourea again shows that q_{zz} derived from the π-OC versus π-SC LMO's is slightly larger (positive) in the O compounds, although a full analysis with the nuclear component is required to give a detailed picture.

3. Conclusions

We have obtained equilibrium structures with large (TZVP) basis sets at the MP2 correlated level. The resultant wave-functions, the natural orbitals, show that the primary contribution other than the SCF determinant consists of determinants, where one of the σ-MO's is doubly replaced (i. e. both electrons) by a π^*-MO, with resultant loss of some σ-electron density. Hence the total π-occupancy is very slightly above the classical picture of 4π-electrons for an amide group. The molecular structures are close to experiment in the few cases where MW and ED data are available. The tetramethyl urea and thiourea molecules still retain a planar skeleton, but with significant distortion of the CNC and HCN angles, when a gear-wheel conformation is adopted.

The dipole moments are dissected (Fig. 5) in terms of the average positions of the electrons for the NO's, and the push-pull mechanism for the allylic system seems to account for the higher dipole moments in thioamides than amides. The corresponding dissection of the formamidine system, where the electronegativity of the doubly bonded group is the same as that of the 2π-electron donor to the allylic system, shows that the matter is not just a result of the better σ-electron donation of S relative to O, since the same phenomenon occurs in the amidine. It appears to be an inevitable consequence of the 2,1,1-π electron contributions of N,C and O(or S) to the allylic system. The same approach to the urea and thiourea systems, which are perturbed examples of the trimethylenemethane system, is also successful.

The NO's localise readily to LMO's, and these account for the gross magnitudes of the electronic terms in the EFG. However, in the summation with the nuclear terms, the more distant centres still have some defining impact. Hence the general trends for ^{14}N NQCC to be higher in amides than thioamides, do emerge from the LMO analysis.

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