The ab initio Calculation of Nuclear Quadrupole Coupling Constants with Special Reference to ^{33}S *

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The ab initio calculation of ^{33}S nuclear quadrupole coupling constants (NQCC) for a range of S-containing compounds with S^2, S^4 and S^6 bonding types is described. All of the calculations used a triple zeta valence + polarisation basis set (TZVP) of gaussian type orbitals; all of the molecules were studied at the TZVP equilibrium geometry. The electric field gradients (EFG) calculated were correlated with the experimental NQCC obtained by either microwave spectroscopy (MW), nuclear quadrupole resonance (NQR) or NMR relaxation methods; although the experimental data cover a wide diversity of chemical types over a long period of time, the slope of the relationship between the EFG (q_{ii}) and the NQCC (χ_{ii}) yields a value for the ^{33}S atomic quadrupole moment of -0.064 barn, very close to recent calculations with a large atomic basis set, and to experimental data.

The relationship between the EFG tensor components and the internal molecular structure features is discussed for a diverse series of molecules.

1. Introduction

In previous papers at this series of NQR Conferences we have discussed the quadrupole coupling of single molecules; hence these are to be compared with gas phase data, containing ^{14}N and ^{11}B nuclei [1, 2]. If ^{14}N is omitted from consideration, the most important biological molecules have oxygen and sulphur in their structures; a study of ^{17}O and ^{33}S NQCC is thus important. Unfortunately, the natural abundance of these two isotopes is only 0.037% and 0.760% of the total O and S atomic matter, and their respective spin quantum numbers are 5/2 and 3/2, respectively. Relatively few such molecules have been studied by microwave spectroscopy although there are many examples of structures with the common ^{32}S nucleus. With the advent of Fourier transform microwave spectroscopy (FT-MW) it should be possible to rapidly generate the ^{33}S and ^{17}O data from these earlier ^{32}S and ^{16}O studies. Furthermore, such studies will refine the structural data further by giving more isotopic combinations. NQR studies of ^{33}S and ^{17}O are also relatively few in number, but again we might hope for increased activity in that area; unfortunately, only the relative magnitudes (i.e. no signs or directions of the tensor elements) are obtained from NQR data, and all of the group resonances are essential for secure assignment, especially if more than one quadrupolar centre is present. Use of the La Place relation (trace of elements in zero) is dangerous when (say) 4 out of 6 nitrogen frequencies are observed in cases where 2 different centres are present; this is commonly the case for nitrogen in particular.

Another area is becoming increasingly active for nuclear quadrupole coupling constant determination, namely NMR studies in solution; as described below, line width and relaxation time studies yield values of the largest NQCC tensor element, but usually neither the sign nor the dircetions or the asymmetry.

It should be noted that MW data lie in the inertial axis (IA) frame, where it is traceless; unless the molecular inertial axes lie parallel to molecular symmetry axes, these IA values will not correspond to the electric field gradient (EFG) principal axes, in which the NQR data are obtained. Hence there are two different axis systems to be considered.

Thus in the present paper we consider many of these ^{33}S cases where experimental data are available in order to find what level of theoretical investigation is necessary to bring out the main features of their cou-

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pling in electric field gradient principal axis systems (EFG-PA).

Early reviews of ^{17}O and ^{33}S nuclear quadrupole coupling results from NQR and MW spectroscopy were given by Lucken [3] and Edmonds [4]; the systems studied form a rather random group of chemical structures; in the case of the MW data, the small molecular systems show some symmetry, and hence the inertial and EFG principal axes can be correlated; also the absolute signs are available.

We have studied all the simple systems for which data are accessible, usually at the corresponding equilibrium geometry. It is convenient to consider the molecules in turn, and correlate with structure in a later Section.

2. Theoretical Methods in the Present Study

All of the present calculations used a triple-zeta + polarisation (TZVP) basis of gaussian type orbitals (GTOs), and all molecules were fully optimised for the equilibrium structure with that basis at the SCF level. The exponents used are the Dunning and Huzinaga bases, with each valence shell basis function uncontracted [5, 6]. In some cases a complete active space scf study (CASSCF) was performed with a subset of the occupied and virtual MOs, but generally the studies beyond a single configuration SCF used an all valence electron CI at the SCF optimised structure; thus whilst refinements to the wave-function were incorporated, no structural changes were made at that level. All of the computations were performed on either the RAL or ULCC Cray-XMP computers, using the GAMESS package [7]. The principal results are shown in Tables 1–3 for the total energies of the molecules studied, ^{33}S quadrupole coupling constants and structural features, respectively. In Table 1, the comments refer to the number of active molecular orbitals in the CI (all valence electrons were active), and the number of configurations generated (CSF, configuration state functions). In Table 2, the molecular orientation refers to the axis system shown in the diagrams for the molecular axes; in general, for C_{2v} molecules this will mean the molecule lies in the y,z-plane with C_2 axis in the x,z-plane. The orientation of the EFG principal axes in Table 2 is shown in the diagrams with xx, yy, zz simplified to x, y, z; thus there is a distinction between x, y, z in the molecular orientation and x, y, z in the EFG in most cases.

Table 1. Compounds studied and their total energies at their equilibrium structures.

Compound	Basis set	(TZVP)	Method	Energy (a.u.)	Comments
H_2S	39	SCF	−398.70134		
		CI	−398.87199	8e	29 MO 941 CSF
H_2S_2	66	SCF	−796.23652		
		CI	−796.53621	14e	44 MO 3525 CSF
Me_2S	103	SCF	−476.78868		
		CI	−477.23589	20e	76MO10143CSF
C_2H_4S	91	SCF	−475.59655		
		CI	−475.95698	18e	49 MO 4230 CSF
C_4H_4S		SCF	−551.36130		
		CI	−551.92261	26e	76 MO 6957 CSF
S_8	168 (TZV)	SCF	−3179.92809		
$C_2H_2S_2$ (cyclic)	101	SCF	−871.94212		
		CI	−872.42390	22e	60MO11326CSF
$C_2H_2S_2$ (acyclic)	101	SCF	−871.93185		
		CI	−872.41126	22e	60MO10889CSF
$C_3H_3S_2(+)$	132	SCF	−910.18833		
		CI	−910.82645	26e	97 MO 4348 CSF
$C_5H_5S(+)$	184	SCF	−589.58476		
CS	47	SCF	−435.33925		
		CI	−435.60732	10e	41 MO 4500 CSF
CH_2S	59	SCF	−436.54411		
		CI	−436.81778	12e	36 MO 1947 CSF
OCS	67	SCF	−510.32353		
		CI	−511.64405	16e	37 MO 3229 CSF
SCS	74	SCF	−823.94094		
		CI	−833.34916	16e	52 MO 4278 CSF
HNCS	73	SCF	−490.44794		
		CI	−490.87846	16e	58 MO 8333 CSF
SO	47	SCF	−472.36412		
		CI	−472.62284	10e	28 MO 3331 CSF
SO_2	67	SCF	−547.23766		
		CI	−547.60374	18e	45 MO 4474 CSF
S=S=O	74	SCF	−869.88438		
		CI	−870.35823	18e	51 MO 8801 CSF
SO_3	87	SCF	−622.07172		
	63	SCF	−621.75548		
	63	CI	−622.43622	24e	40 MO 5834 CSF
SF_2	67	SCF	−596.41585		
SF_4	107	SCF	−795.31288		
		CI	−795.67675		
SF_6	147	SCF	−994.22719		
		CI	−994.68933	48e	63 M 57409 CSF
SCl_2	81	SCF	−1316.52767		
Me_2SO	123	SCF	−521.61751		
		CI	−552.07846	26e	65 MO 5489 CSF
$C_2H_4SO_2$	131	SCF	−625.25358		
		CI	−625.76927	28e	68 MO 4659 CSF
Me_2SO_2	143	SCF	−626.48835		
		CI	−626.96161	28e	71 MO 6439 CSF
Cl_2SO	101	SCF	−1391.36920		
		CI	−1391.83176	26e	48 MO 6138 CSF
Cl_2SO_2	121	SCF	−1466.21490		
		CI	−1466.68885	30e	56 MO 6453 CSF

Table 2. ^{33}S nuclear quadrupole coupling constants (a.u.) at equilibrium.

Compound	Method	χ^2	Y^2	Z^2	η	Molecular orientation
H_2S	SCF	2.49099	−2.14922	−0.34163	0.726	yz-plane, $z=C_2$ axis
	CI	2.42457	−2.07317	−2.35148	0.710	
Me_2S	SCF	2.83323	−2.38672	−0.44659	0.685	C_{2v}, yz-plane
	CI	2.77615	−2.33304	−0.44320	0.681	
C_2H_4S	SCF	2.91872	−1.01820	−1.90061	0.302	yz-plane, $z=C_2$ axis
	CI	2.84892	−0.99000	−1.85900	0.305	
C_4H_4S	SCF	1.53043	−1.93339	0.40228	0.583	yz-plane, $z=C_2$ axis
	CI	1.50298	−1.89459	0.39153	0.587	
H_2S_2	SCF	2.95876	−0.31003	−2.64881	0.790	
	CI	2.88905	−0.31304	2.57610	0.783	C_2 S−S axis parallel to y
$C_2H_2S_2$ (cyclic)	SCF	2.97431	−0.23852	−2.73497	0.840	z is C_2 axis in yz-plane
	CI	2.91557	−0.24237	−2.67328	0.834	
$C_2H_2S_2$ (acyclic)	SCF	−2.43067	3.05248	−0.62189	0.593	z is C_2 axis in yz-plane
	CI	−2.36377	2.97666	−0.61298	0.588	
$C_3H_3S_2^+$	SCF	1.58897	0.60959	−2.19865	0.445	yz-plane, $z=C_2$
	CI	1.55768	0.59323	−2.15099	0.448	
$C_5H_5S(+)$	SCF	0.43102	−1.43361	1.00251	0.339	C_{2v} yz-plane, $z=C_2$ axis
CS	SCF	−0.34390	−0.34390	0.68772	0.0	
	CI	−0.33405	−0.33405	0.66802		
CH_2S	SCF	−2.23792	2.89691	−0.65907	0.545	yz-plane, $z=C_2$ axis
	CI	−2.23650	2.84395	−0.60753	0.573	
SCS	SCF	0.52503	0.52503	−1.05015	0.0	z-axis
	CI	0.51585	0.51585	−1.03178	0.0	
OCS	SCF	1.02987	1.02987	−2.05982	0.0	z-axis
	CI	1.00595	1.00595	−2.01197	0.0	
HNCS	SCF (opt.)	0.92247	−2.11804	1.19548	0.129	C_s, xy-plane
	CI	0.90278	−2.08119	1.17833	0.132	
HNCS	SCF (MW)	0.41360	−1.74287	1.32919	0.525	C_s, xy-plane
SO	SCF	0.22493	0.22493	−0.44976	0.0	z-axis
	CI	0.25088	0.25088	−0.50175	0.0	
OSO	SCF	−2.12674	−0.02118	2.14783	0.980	yz-axis, $z=C_2$ axis
	CI	−2.03328	−0.02060	2.05380	0.980	
$S_{(1)}S_{(2)}O$	SCF (S1)	2.10599	−0.26183	−1.84424	0.751	xy-plane C_s
	CI (S1)	2.02809	−0.27578	−1.75240	0.728	
	SCF (S2)	2.53241	−1.35318	−1.17932	0.069	
	CI (S2)	2.46967	−1.32638	−1.14337	0.074	
SO_3	SCF	0.83100	0.83100	−1.66200	0.0	xy-plane D_{3h}
	CI	0.81470	0.81470	−1.62951	0.0	
SF_2	SCF	5.74631	−3.97369	−1.77270	0.383	C_{2v}, yz-plane, $z=C_2$ axis
SF_4	SCF	−1.09501	−1.58022	2.67515	0.181	C_{2v}, lone pair along z-axis
	CI	−0.93213	−1.50353	2.43556	0.235	
SCl_2	SCF	4.80289	−3.30286	−1.50011	0.375	C_{2v}, yz-plane, $z=C_2$ axis
Me_2SO	SCF	2.20470	−1.02193	−1.18285	0.073	C_s, in xy-plane
	CI	2.17138	−0.99731	−1.17415	0.081	
Me_2SO_2	SCF	0.34326	−0.22671	−0.11664	0.321	C_{2v}, x axis o.o.p. to SC_2
	CI	0.34853	−0.23945	−0.10915	0.374	
Cl_2SO	SCF	2.83555	−1.10857	−1.72707	0.218	C_s, in xy-plane
	CI	2.75052	−1.08007	−1.67053	0.215	
Cl_2SO_2	SCF	1.41881	−1.05556	−0.36263	0.489	C_{2v}, xz-bisects SCl_2
	CI	1.38351	−1.03270	−0.35089	0.493	
F_3PS	SCF	1.02233	1.02233	−2.04473	0.0	C_{3v}, z-axis

Table 3. Geometric parameters of compounds studied (TZVP basis) at equilibrium.

Molecule	Bonds (Å)		Angles (°)	
CS	CS	1.5183		
CS_2	CS	1.5460		
OCS	CS	1.5715	CO	1.1235
SO	SO	1.4617		
SO_2	SO	1.4209	OSO	117.651
SO_3	SO	1.4082		
SSO	SS	1.8779	SO	1.4431
			SSO	116.845
CH_2S	CH	1.0779	CS	1.5999
			HCS	122.059
H_2S	SH	1.3333	HSH	94.384
H_2S_2	SH	1.3517	SS	2.2522
$(CH_3)_2S$	CH	1.0816	CS	1.8157
	CSC	100.025	ALPHA[a]	2.5496
	XCH C_{3v}	109.736		
C_2H_4S	CH	1.0735	CS	1.8218
	CC	1.4724	HCS	114.953
	CSC	47.670		
$C_2H_4SO_2$	CH	1.0738	CS	1.7370
	CC	1.5743	SO	1.4412
			CSC	63.053
C_4H_4S	CS	1.7292	C(2)C(3)	1.3438
	C(3)C(4)	1.4347	C(2)H	1.0694
	C(3)H	1.0720	HCS	120.415
	HC(3)C(2)	123.635	CSC	91.098
$C_3H_3S_2(+)$	CC	1.3757	CH(2,5)	1.0744
	CH(4)	1.0711	CS	1.6812
	CCC	114.686	CCS	118.019
	CSS	94.638	SS	2.0446
$(CH_3)_2SO$	CH	1.0815	CS	1.8058
	SO	1.4983	CSC	98.136
	ALPHA[a]	1.7036	XCH	108.764
$(CH_3)_2SO_2$	CH	1.0804	CS	1.7833
	SO	1.4447	CSC	104.564
	OSO	119.412	ALPHA[a]	2.3145
	XCH	108.316		
Cl_2SO	SCl	2.0726	SO	1.4308
	ClSCl	97.709	OSCl	107.268
Cl_2SO_2	SCl	2.0203	SO	1.4133
	ClSl	100.872	OSO	122.599
F_3PO	FP	1.5235	PO	1.4262
	FPO	117.328		
F_3PS	FP	1.5328	PS	1.8734
	FPS	118.440		

[a] ALPHA is outwards bending of local C_3 axis of CH_3 group.

3. Results and Discussion

3.1. The ^{33}S Atomic Quadrupole Moment (Q_S)

The electric field gradient tensor elements (q_{ii}) were evaluated from both the SCF and Cl wave-functions. These EFG elements are linearly related to the observed NQCC (in MHz) by means of the equation

$$\chi_{ii} = 15.14\, q_{ii} - 0.1771$$

with standard deviations in slope, intercept and overall of 0.6627, 1.093, and 4.576, respectively.

The most recent value for the ^{33}S atomic quadrupole moment is $-0.0678(13)$ barn [8] from multi-configurational SCF calculations on the S anion; a recent review of many nuclear moments [9] cites values of $-0.064(10)$ and -0.084 barn from micro-wave absorption and fast-beam laser spectroscopy, respectively. As will be seen below, the correlation of our theoretical values for q_{ij} with the experimental χ_{ij} leads to a value closer to the lower magnitude, but the basis set does not return 100% of the expected value based upon experience with ^{14}N and ^{11}B [1, 2]; so the higher value may be closer to the best value. The matter is discussed below, whilst for the moment, the q versus χ relationship is treated as an empirical scaling matter; the correlation is shown in Figure 1. Because of the grouping of points, it is impracticable to label points in the Figure, but they can be identified from Table 2.

3.2. The Overall Picture from the Correlation of Calculation and Experiment

The survey shown in Fig. 1 shows that generally there is qualitative agreement between the two series of data; it has to be born in mind that the experimental data are derived from diverse sources over some 30 years, and that two main experimental methods MW and NMR have been used; thus whilst most of the measurements are close to room temperature, there will be various levels of inaccuracy in these data. The calculated data are all at the single configuration equilibrium geometry level; thus, if in some particular cases the theoretical structure departs from the gas or solution one, then divergences are to be expected. There is no account of solvent effects on the NMR data either. Overall then, the correlation seems satisfactory.

The correlation line then has a slope of 15.141 MHz/a.u. and the y-intercept is -0.177. Thus, the apparent value of the ^{33}S atomic nuclear quadrupole coupling constant is -0.064 barn, very close to the value of Sundholm and Olsen [8]; however, we have noted previously with respect to ^{11}B and ^{14}N coupling that the TZVP basis returns only about 88% of the ^{14}N value of Q_N; if the same occurs here, and the limitations of the basis set might make a larger error, then a value near -0.073 barn might be more realistic. This would lie near the mean of the best atomic

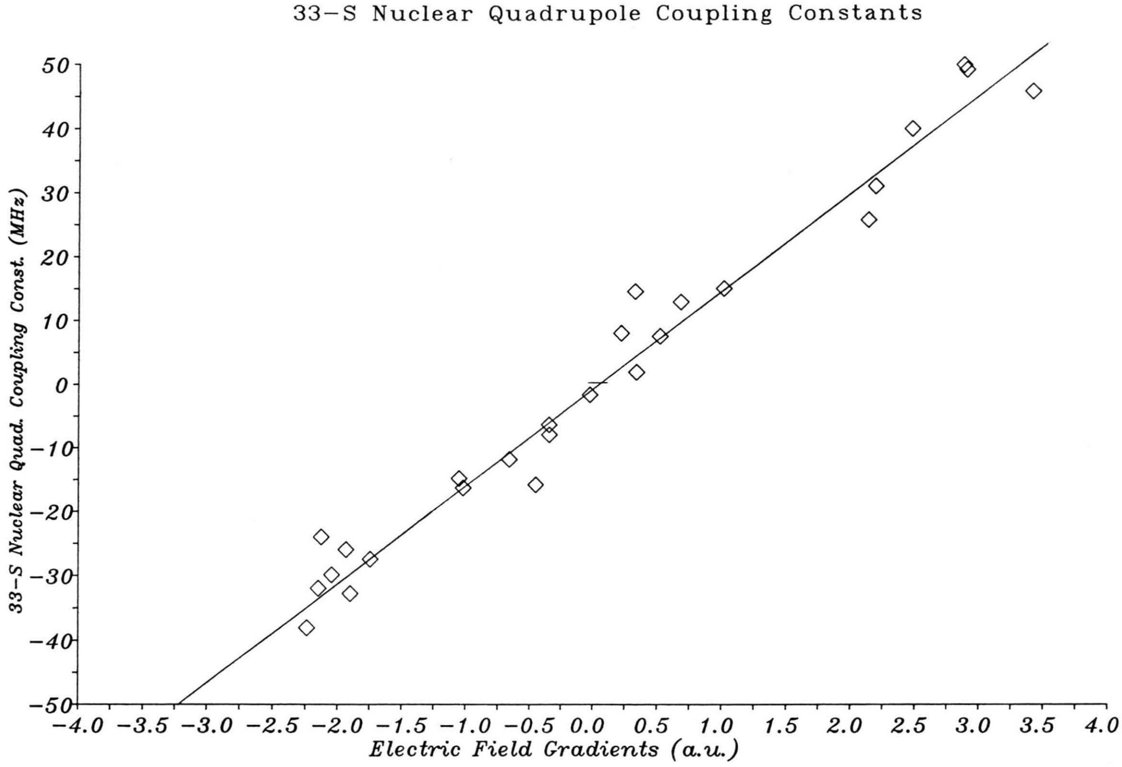

Fig. 1.

calculation and the recent experimental value for the sulphide anion.

3.3. Structural Features and ^{33}S Nuclear Quadrupole Coupling Constants (NQCC)

3.3.1 Bi-covalent Sulphur S^{II}

We start with compounds where sulphur forms two sigma bonds of largely classical type, and then continue with doubly bonded systems.

The simplest case where experimental information is available is hydrogen sulphide (**1**) [10]; although very early determinations, these are still quoted and yield the tensor elements χ_{aa} -32, χ_{bb} -8 and χ_{cc} 40 MHz, respectively; thus the largest value is the local π-direction; some re-determination of these values is indicated by the recent ^{33}S NMR lineshape analysis which yielded 49.0(3.5) MHz, a significantly larger value [11]. The present equilibrium structure shows (Table 2) a structure close to that of the MW one [12], which has HS 1.336 Å and HSH 92.1°; the asymmetry parameter is somewhat larger than the MW value (0.726 versus 0.512), but the order of tensor elements in relation to the *a*, *b*, *c*-axes is the same. Clearly, χ_{cc}, the π-component is largest, and none of the values are changed significantly by all-valence CI; this is in agreement with earlier large basis set and CI studies of hydrogen sulphide [13–15]; it is worth noting here that these authors use Q_S -0.055 barn in their scaling, which is certainly low by current standards.

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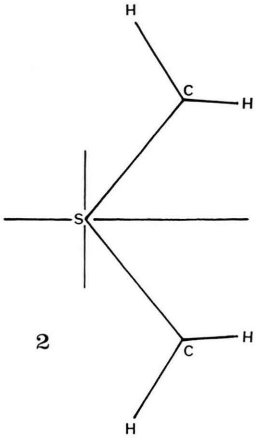
A simple derivative is dimethyl sulphide (**2**), where the MW structure has been known for many years; it has long been assumed that the C3 axis of the pair of



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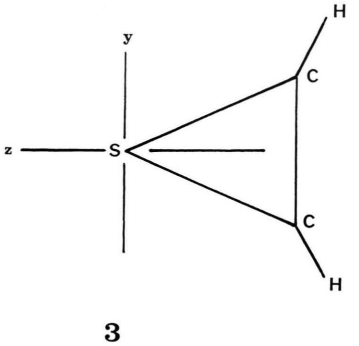
methyl groups is alligned with the C–S bonds [16]; much work on related compounds shows that this is unlikely [17]. In the present study we allowed the C3 axis to deviate from the C–S bond as well as optimizing all other variables; the final result shows that the methyl groups are tilted outwards by 2.550°. All the other variables are relatively close to the MW studies, but the effect is that the CSC angle is about one degree larger than the experimental one, and CS longer by 0.01 Å. The individual NQCC are all slightly larger in magnitude for Me_2S than H_2S, but the tensor element order lies in the same directions, with the π-value being largest.

The cyclic sulphide thirane (**3**) has been analysed for ^{33}S coupling [18]; again the largest magnitude of the tensor lies out-of-plane (χ_{cc}), and larger in magnitude than in C_2H_6S (**2**). In our hands the TZVP structure is slightly smaller in the CSC angle (47.7 against 48.5°), with consequential slight shortening of the CC bond by 0.02 Å. These changes are insufficient to lead to any major changes in calculation of the ^{33}S NQCC, and we obtain values in the same order as the MW ones [18], and η rather similar.



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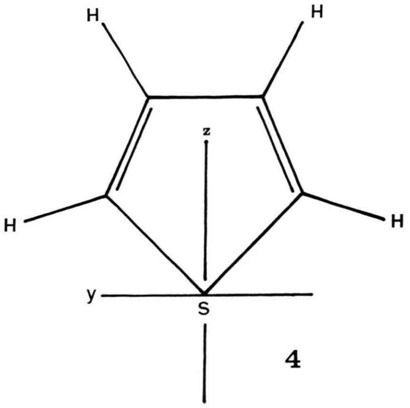
The change from acyclic to strained cyclic, in going from C_2H_6S to C_2H_4S (**3**), leads to little change in the out-of-plane (o.o.p.) value (χ_{cc}), so there is little case in arguing that there is any aromatic character in C_2H_4S (**3**); however, there is a significant change in the in-plane values, with a marked increase in the axial value (χ_{aa}) in the cyclic system, and hence reduction in the transverse (χ_{bb}). This indicates some change in the lone-pair density and suggests that the nucleophilic character of the two molecules should be different. We have also investigated the NQCC in thiophen, C_4H_4S (**4**), an aromatic system, where substitution predominates in electrophilic attack and NMR measurements indicate a ring current; there is a marked reduction in the π-NQCC relative to dimethyl sulphide, such that the largest magnitude now lies in-plane, and along the external bisector of the CSC angle. These conclusions are in agreement with earlier calculations on thiophen [19]. The radial term is small, but of opposite sign to that in dimethyl sulphide. The π component is almost halved in magnitude relative to thirane (**3**). There are no MW data for thiophen as yet, but ^{33}S relaxation time measurements suggest that the principal quadrupole axis coupling is 26 MHz [20], almost half that of thirane, and in agreement with the present calculations. The assumption that the principal axis for the relaxation measurements lies normal to the CSC plane is in agreement with this work.



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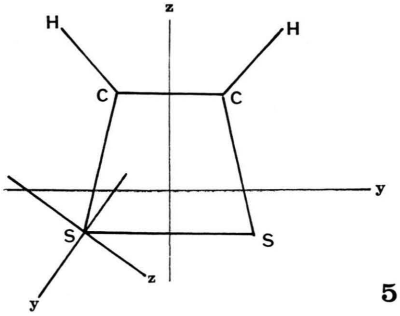
Recently, the MW spectrum of 1,2-dithiete (**5**) was reported [21]; this molecule is of interest since there is an open-chain form, ethane-1,2-dithione (**6**); it is not correct to regard these as tautomeric structures, as was apparently done in a earlier theoretical study [22], because the latter has only a 4π electron valence shell, while the 1,2-dithiete is a 6π valence shell; hence interconversion requires a $\sigma-\pi$, from a b_2 to a b_1 MO,



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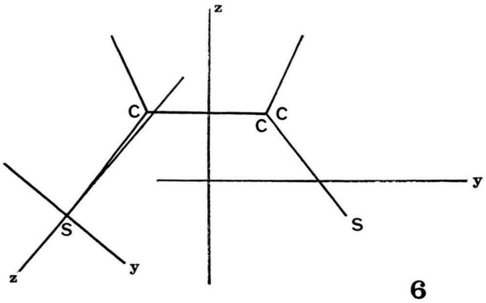

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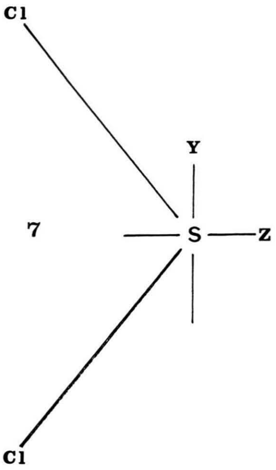
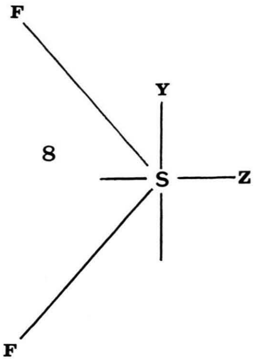
switch of electrons. Strictly then, one is a doubly excited state of the other; Rodler and Bauder [21] show that the rotation constants observed are more consistent with the cyclic structure (**5**) than the bis-di-thione (**6**). The theoretical equilibrium structures for the isomers at the TZVP basis level show quite distinct structures, the cyclic form has CC 1.322 and CS 1.770 Å, whereas the acyclic form has CC 1.483 and CS 1.604 Å, rather as expected from the interchange of long and short bonds; in [22] the energy differences are very dependent on the basis set. The TZVP total energies at the SCF level showed a difference of 0.28 eV, with the cyclic dithiete lower in energy; when an all valence Cl was performed at the same geometries, the corresponding figures were 0.35 eV, so little difference occurs when the basis is large. The quadrupole couplings are also quite distinct, the direction pointing towards the interior of the ring (radial direction) (**5**), which is the lowest tensor magnitude lies about 22° from the CS bond; in the acyclic system (**6**), where the effect of the non-attached –CHS group is much smaller, the divergence from the bond axis is smaller. The dithione structure effectively behaves as two separate units for NQCC effects.

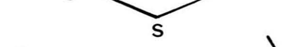
The simplest sulphur halides, SF_2 (**7**) and SCl_2 (**8**) have been investigated by MW spectroscopy [23, 24], but the ^{33}S couplings not yet reported. The present results at the TZVP basis set level, and equilibrium geometry as usual, show that the values of χ_{ii} will be much larger than in either H_2S (**1**) or Me_2S (**2**). All the couplings are doubled for the di-fluoride, relative to H_2S. There is a progressive increase in values between the H, Cl and F substituents of the series X_2S, indicating the effects of polarity of the substituent. The largest NQCC in each of these X_2S structures is out-of-plane.





3.3.2. Bi-covalent Sulphur S^{II} with more than one S Atom

The parent element sulphur (**9**) occurs as individual molecules of S_8 in D_{2D} symmetry, basically two squares of S atoms separated by about 0.49 Å along the *z*-axis and rotated between the squares by 45° [25].



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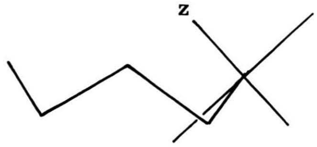
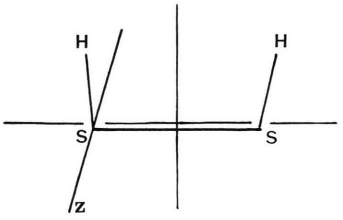


9B

Using the TZVP basis, we found the SCF optimization of the structure, even with only 2 variables, very time consuming; the basis set contained 216 GTOs, and calculations at the crystal structure showed the d-functions to contribute relatively little. Hence the main study was performed with a TZV basis, i.e. as in TVZP but without the d-functions (168 basis); strictly the EFG scaling factor will be different, owing to a changed value for Q_S for this basis; however, the principal reason for the study is to identify the axis orientations in S_8. We find the principal axes are the internal and external bisectors of the SSS angle, with the largest value in the local π-direction; this latter axis is tilted outwards by about 11° from the SSS local plane. The NQR value for the ^{33}S coupling has been known for some time [26], at 45.8 MHz, and was used to determine an early value to Q_S of $+0.035$ barn. It is clear that the sign of the NQR value for S_8 is positive.

A further molecule with classical single bonds to bivalent sulphur is hydrogen disulphide (H_2S_2) (**10**).

10A



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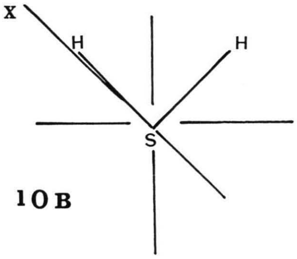
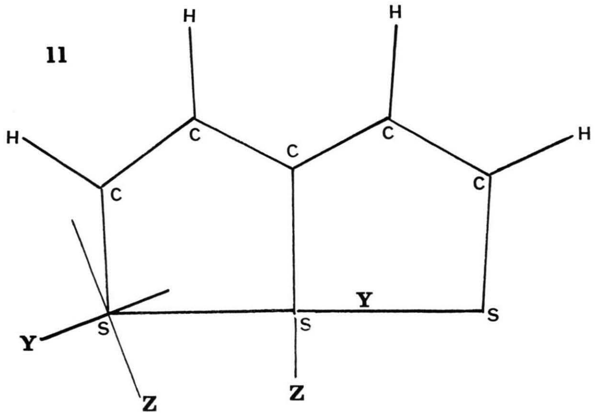
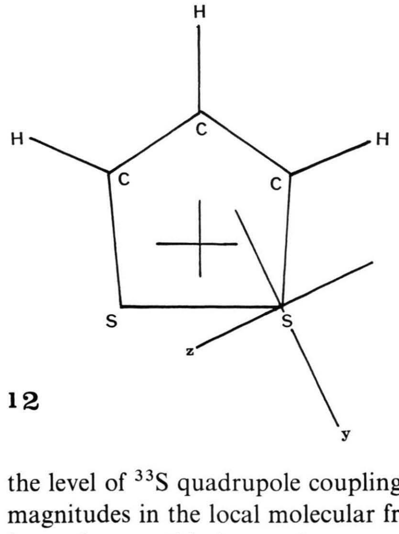


There have been a number of MW studies, but no ^{33}S NQCC so far measured; the molecule has C_2 symmetry, with the atoms lying on two planes at an angle of about 89.9° (calc.) or 90.6° (MW) [27]. The MW spectrum is complex, and a series of further investigations have concentrated on the Q branches etc., but no further refinements to the structure have emerged. We find the bond lengths very similar to the MW values, but the HSS angle differs from experiment (91.5°) at 98.5°. If the molecule is regarded as a perturbed S_2 molecule lying in the z-axis, then the H atoms lie very close to the x, y-coordinate axes; in the limit of large HS distance, the NQCC would have cylindrical symmetry; in the present structure, we find the largest value of the NQCC lies nearly perpendicular to the attached SH bond, while the smallest value lies fairly close to the SH axis; thus the formation of two bonds at right angles leads to a fundamental switch of NQCC axes from the axial symmetry of the dimeric S_2 molecule.

For many years reactivity studies, where substitution is more frequent than addition, has been used to argue that aromaticity is important in thiathiophthen (**11**) (1,6,6a-triazapentalene series) [28], 1,2-dithiolium cations (**12**) [29] and thiapyrylium cation (**13**) (**26**) [30]. Thiathiophthen (**11**), 1,2-dithiolium cation (**12**) and thiapyrylium cation (**13**) are planar systems. Clearly the level of ^{33}S quadrupole coupling and the relative magnitudes in the local molecular frame will give information on this issue; there are no experimental data so far, but NQR studies of the ionic solids can be anticipated.

11





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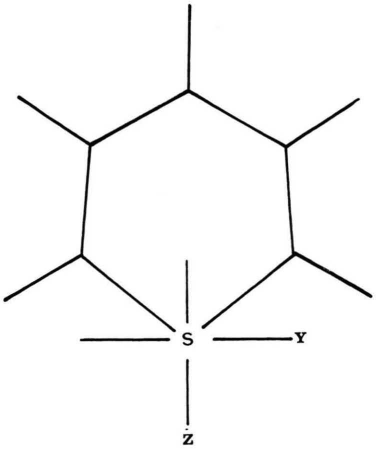
The principal axes of the NQCC in the thiapyrylium (**13**) and dithiolium cation (**12**) are almost radial



13

and tangential at the S atoms, with the largest value as external bisector of the SSC angle; there is a considerable similarity to the tensor elements in thiophen, but the values in the π-directions are somewhat variable. The terminal pair of S atoms in thiathiophthen (**11**), are rather similar in environment to both 1,2-dithiolium cations (**12**), but the tensor elements are rotated by about 45° between the two molecules. The central S atom of thiathiophthen (**11**) is effectively a trigonal bipyrimid, since localised orbital calculations show the presence of two lone pairs ($\sigma+\pi$) [30]. Thus this atom in (**11**) is more closely related to that in SF_4, and is covered in a section below.

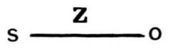
As yet there is no experimental information, but we might expect that measurements of the ^{33}S coupling in aromatic type heterocycles will vary with the electron delocalisation to the C atoms.

3.3.3. Doubly Bonded ^{33}S Nuclei

3.3.3.1. Linear and Cumulative Molecules

One of the simplest molecules where there are ^{33}S data is sulphur monoxide (**14**). The MW spectrum of this triplet state molecule shows χ_{zz} −15.9 MHz [31]; we have studied the molecule at the corresponding restricted Hartree-Fock (RHF) level, i.e. doubly occupied MOs (except for the 2 unpaired spins). The equilibrium structure under these conditions has an SO bond length of 1.4617 Å, to be compared with 1.4810 Å [31]. As in the oxygen molecule case, the lowest energy triplet is the $\pi_x-\pi_y$ triplet, and the singlet is about 0.17 a.u. (450 kJ mol^{-1}) above this. The EFG-PA corresponding to this value (−15.9 MHz) is along the molecular axis. Closely related to SO is another diatomic molecule, CS (**15**) (a singlet ground state); the ^{33}S coupling is found to be 12.835 MHz [32]; the present calculations give a good correlation at both SCF and Cl levels for this molecule, where again there is axial symmetry; the bond length is calculated to be 1.5182 Å, to be compared with the MW value of 1.5349 Å [33].

14



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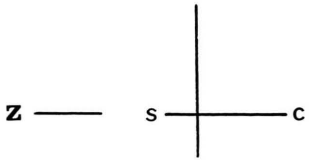
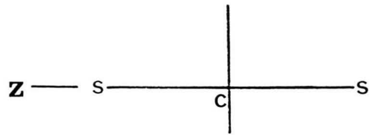


Carbon disulphide (**16**) has been studied by NMR methods [34, 35]; the results, 13.8 (1.4) [34] and 14.9 (0.3) MHz [35] correlate quite with the present TZVP results, providing the sign is negative. This assumption is reasonable since the sign of the ^{33}S coupling for carbonyl sulphide (OCS) (**17**) is long known to be negative [36, 37] from MW spectroscopy. Disulphur monoxide (S_2O) (**18**), has a central S atom very similar in environment to that of SO_2, but the terminal S atom has the EFG-PA rotated strongly from the SS bond.

16



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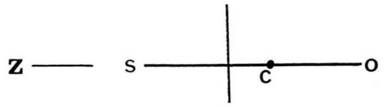

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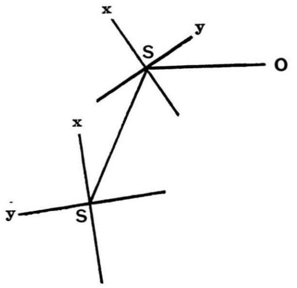
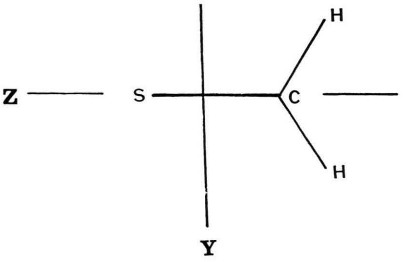


Although not strictly related to the thiocarbonyl compounds above, the thiophosphoryl compound, trifluorophosphine sulphide, for which the C_{3V} structure and ^{33}S NQCC have been obtained [38, 39], also shows a negative axial value (−29.924 MHz); this correlates well with the present calculations in Figure 1.

3.3.3.2. Thiocarbonyl Compounds

Thioformaldehyde ($CH_2{=}S$) (**19**) has to be made in situ for spectroscopic measurements, owing to high reactivity; the present MO calculations show that it has a particularly low first virtual (antibonding-π) level; hence thermal conversion to the 1,3,5-trithiane 6-membered ring is facile. The microwave spectral values for the ^{33}S quadrupole coupling constants [40] which have recently been refined [41] show a low value along the C−S bond (χ_{aa} −11.898 MHz) with another larger in-plane value (χ_{bb} +49.981 MHz) and out-of-plane (χ_{cc} −38.083 MHz).

19



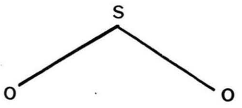
It is of interest to compare the values of these quadrupole couplings for CH_2S with those for formaldehyde ($CH_2{=}O$); the inertial axis alignments are the same for both molecules, and the IA are coincident with the principal electric field gradient axes. The NQCC for ^{17}O in formaldehyde [42] also recently refined [41] yield the values χ_{aa} −1.906, χ_{bb} +12.35 and χ_{cc} −10.45 MHz, respectively. The ratio of the atomic quadrupole moments for the ^{33}S and ^{17}O nuclei is around 3.26 [8], so that the EFG are of similar order in (say) atomic units but show the effects of differing bond lengths and polarities. The ratio of the trifluorophosphine sulphide to oxide adduct [38] NQCC at S and O is similar to that of thioformaldehyde to formaldehyde, when the Q_S to Q_O ratio is included; hence the bonding is probably rather similar in C=S and C=O, relative to P=S and P=O.

A number of other thiocarbonyl compounds have been investigated at equilibrium for ^{33}S NQCC [43], using a double zeta + polarisation basis; the values are about 50% larger in magnitude than the present TZVP basis, implying a much lower value for Q_S; the direction of the tensor elements are not given in [43].

3.3.3.4. Tetra-covalent Sulphur S^{IV}

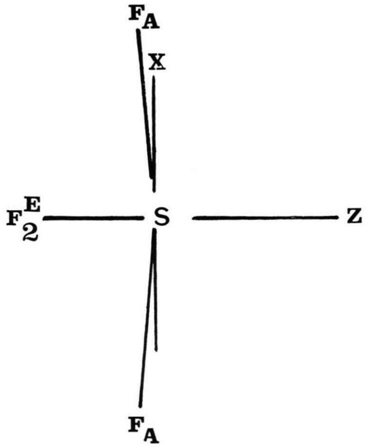
Sulphur dioxide (**20**), where the ^{33}S is central, and which also has a classical lone pair of electrons, has a positive ^{33}S coupling in the molecular plane χ_{bb} is 25.71 MHz with η 0.87 [44]. Thus two of the couplings are of similar magnitude but opposite sign; these are in the lone pair and π directions. A previous study of SO_2 [45] gave rather higher values for all the EFG elements but did show the very close magnitudes of two of the terms.

20



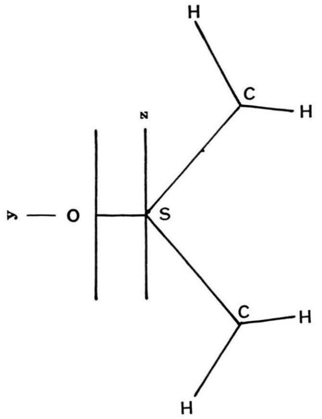
Sulphur tetrafluoride (SF_4) (**21**) has a trigonal bipyrimid structure with the lone pair in the equatorial triangle [46]; the structure is only of C_{2v} symmetry [46]. We obtain the largest ^{33}S quadrupole coupling close to the lone pair direction. The molecule has a significant difference in the SF axial (long) and equatorial (shorter) bonds, and the $F_{ax}SF_{ax}$ angle is nearly linear. The Cl has a more marked effect on this wavefunction than other members of the present series.

21

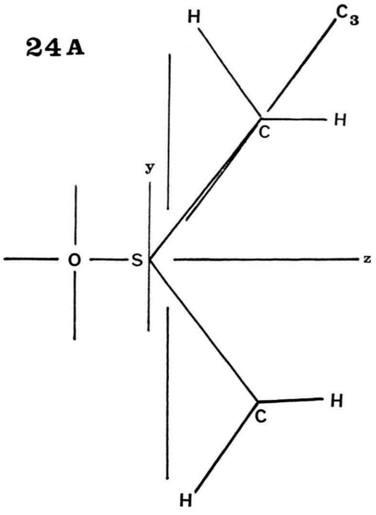


Finally, we consider the two simplest types of sulphoxide, where the substituents are an electron donor (di-methyl) (**22**) and acceptor (di-chloro) (**23**); both di-methylsulphoxide (**24**) and thionyl chloride (**25**) are pyramidal molecules [47–50]. Again, the methyl groups cannot be assumed to have their C_{3v} local axes alligned with the CS bonds; we find the outwards bend of the axis to be 2.3144°; however, this bend was constrained to be only outwards versus inwards, and a further variable might be non-zero,

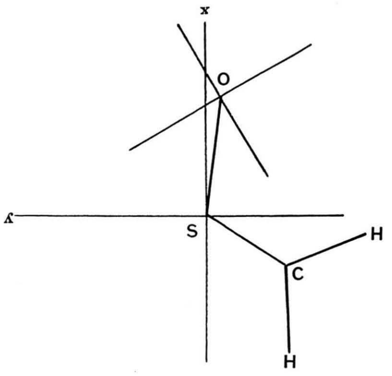
22 A



24 A



22 B



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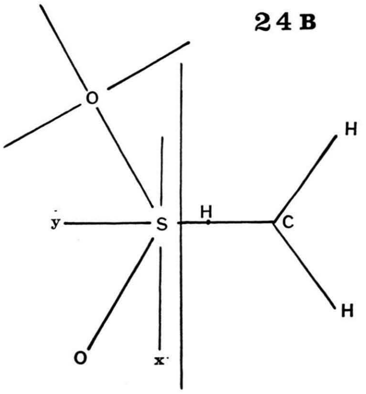
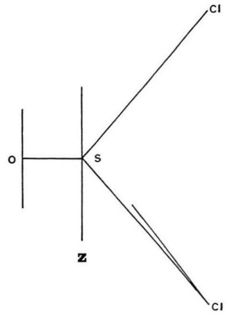
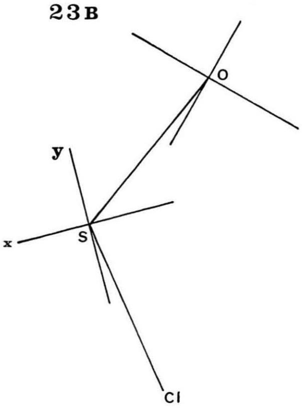


23 A



23 B



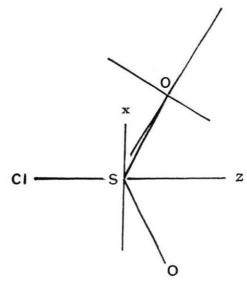
namely the up-down bend in the pyrimid sense. The calculated structure for dimethyl sulphoxide is slightly smaller in CS and SO bonds by about 0.01 to 0.02 Å in both cases when compared with the early MW structure; however a revision of the latter seems worth completing. The ^{33}S quadrupole coupling has the maximum value pointing in the general direction of the lone-pair, but distorted from the pyramid direction by about 45°. In the dimethyl compound χ_{zz} is rotated towards the O atom, along the C_2 symmetry axis, while the other value in the symmetry plane (xy) is close to the SO axis. In the chloro compound ($SOCl_2$), χ_{yy} lies about 53° away from the SO axis, and hence more towards the Cl–S axis. All of the tensor elements are larger in the chloro- than in the methyl compound, but the order of magnitudes follows approximately the same orientations. There are no MW data on these two compounds, but some previous NMR studies of relaxation assumed a value for the largest element of -31 MHz from a somewhat smaller series of basis sets from the present work, for the dimethyl sulphoxide system, by use of H_2SO as a model system [48].

If the lone pair of sulphur dioxide (**22**) is removed by oxidation to sulphur trioxide, the EFG-PA is now o.o.p., and the value computed -1.050 a.u. is to be compared with -2.127 a.u. for the π-direction of sulphur dioxide. Both molecules have the same sign for the o.o.p. tensor element, but the trioxide value is expected to be about half of that for the dioxide.

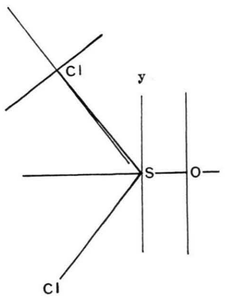
3.3.3.5. Six-covalent Sulphur S^{VI}

The simplest compound of this type is sulphur hexafluoride (SF_6); the regular octahedral structure means that there is no ^{33}S NQCC. Sulphuryl chloride (O_2SCl_2) (**24**) and dimethyl sulphone (Me_2SO_2) (**25**) have also been studied; there is a lack of experimental data, but NMR measurements of relaxation in tetramethylene sulphone (sulpholane) suggest that a reasonably samll value of 1.34 MHz ($\eta = 0.56$) is consistent with the NMR data [51]. The present calculations on both molecules show very small couplings, consistent with experiment. The MW structure of thirane-1,1-dioxide, the 3-membered ring sulphone (**26**), shows a CSC angle of 48.8° [52]; we obtain 49.2°. The ^{33}S coupling is interesting in showing a reversal of order of the tensor elements relative to dimethyl sulphone; the thirane sulphone has the largest value in plane, the acyclic case has the o.o.p. value largest in magnitude; further, the two in-plane values are switched, such that the largest value lies along the OSO bisector (here the C_{2v} axis).

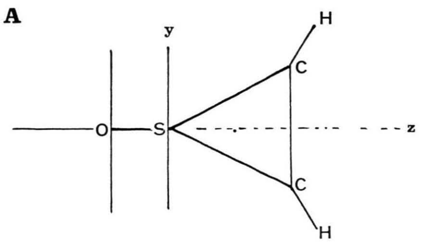
25A



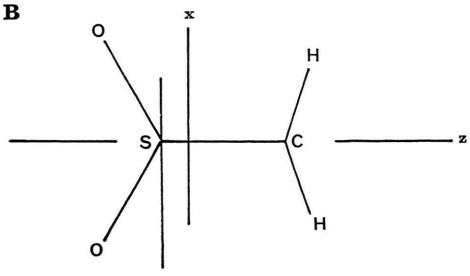
25B



26A



26B



4. Conclusions

The present TZVP basis gives a reasonably good account of the ^{33}S NQCC observed with a diversity of molecular systems; in almost all of the cases studied the results were calculated at the equilibrium structure; hence any inadequacy of the TZVP basis in the SCF variation of the geometry will probably lead to a built-in discrepancy; in the cases studied, the only one where the SCF geometry is known to be widely inaccurate is HNCS (**29**), isothiocyanic acid; in that case, adoption of the MW structure improves the agreement with experiment for the NQCC. As satisfactory feature of the calculations, is that all-valence electron Cl has little effect upon either the tensor elements individually, or on the asymmetry parameter. This indicates that the TZVP basis single configuration study is well behaved.

The correlation shown in Fig. 1, is sufficiently good for predictions of ^{33}S quadrupole couplings to be predicted for many molecules, and this has been done in the present paper. The signs of NQR and NMR values can be determined with certainty, provided that η is low. The high positive values of χ correspond to directions (in general terms) where there is a high lone-pair character; this will include local π systems as in H_2S (for the o.o.p. element), S_8 for the similar direction, the transverse in-plane values in thio-ketones, and cases like the central S atom of thiathiopthen.

There is a cluster of negative values observed near −30 MHz, but these form a rather more diverse group.

There is no doubt that for many cases, NMR measurements give useful data for ^{33}S couplings, although the absence of sign, direction and asymmetry parameter make the information less valuable than MW studies. There is urgent need for reinvestigation to many S containing structures by MW spectroscopy, and FT-MW can be expected to make a major contribution. The success of ab initio calculations of the present level, to at least give reasonable agreement with experiment, means that theoretical predictions can be relied upon in most cases, with perhaps the obvious exception of cases where the two tensor elements are close in magnitude, in which case the NQR order $\chi_{zz} > \chi_{yy} > \chi_{xx}$ will not necessarily be obtained.

The approach here is quite different to that adopted in some other work [52], where variable basis sets (i.e. different quality for different atoms) were used within one molecule; the purpose of that approach was a necessary expediency in computational effort; it was desired to compute the EFG to high accuracy in a particular environment, but not be able to utilise that basis size across the whole molecule. Whilst such an approach will give high accuracy values at the centre when the contributions from the neighbour atoms are small, this will not necessarily always be the case. Furthermore, it is well-known that mismatched bases within a molecule will induce polarisation in the molecule, with resultant distortion of the EFG. Hence we have adopted the approach that all atoms will be treated as similarly as possible, with a consistent basis set across the whole molecule. Here we use a triple zeta valence + polarisation basis. Such basis sets are also balanced between molecules, and hence allow chemical effects, variation of NQCC with structure to be seen more easily. There is clearly a need for both approaches.

A recent measurement of ^{33}S quadrupole coupling by optically detected NQR in a matrix isolated sample of dibenzothiophen [53], suggests another route to couplings in this type of compound.

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