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^{33}S NMR Shieldings and Chemical Bonding in Compounds of Sulfur

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ABSTRACT: *Sulfur nuclear magnetic resonance (NMR) chemical shieldings have been determined at the correlation-including density functional theory scaled B3LYP/6-311+G(nd,p)//B3LYP/6-311+G(d,p) and modified MP2/6-311+G(nd,p) estimated infinite order Møller-Plesset levels with $n = 2$ for sulfur. The calculations span the range of sulfur shieldings and show agreement with experiment of about 3% of the shielding range. The atoms-in-molecules delocalization index and a covalent bond order from specific localized orbitals in the DFT approach are used to characterize sulfur's bonding and to relate it, where possible, to the calculated shieldings.* Heteroatom Chem 15:216–224, 2004; DOI 10.1002/hc.20000

INTRODUCTION

There are not as many nuclear magnetic resonance studies of ^{33}S compared to other nuclei because the sulfur nucleus has a relatively large quadrupole moment that, in asymmetrical environments, leads to very broad lines that make its resonance difficult to detect and characterize quantitatively. It is not uncommon to have line widths reported that are a considerable fraction of sulfur's total range of observed shieldings. A great deal of data is found in the recent reviews of Hinton [1] and Barbarella [2].

Because of the experimental difficulties, theoretical studies have also been somewhat sparse, the recent study by Bagno [3] being a notable exception. Bagno calculated both chemical shieldings and electric field gradients for a wide range of sulfur compounds and compared his results not only to experiment but also to early theoretical work [4–8] carried out in the previous 10 years. Bagno used a Hartree-Fock approach and found rather good agreement with experiment except for SO_2 which shows a very large experimental deshielding. The Hartree-Fock approach does not, by definition, contain correlation and so must be considered somewhat suspect when systems with large and negative absolute shieldings are treated.

Our primary purpose in the present paper is to exhibit shielding calculations with two correlation-including methods, a modified density functional theory approach [9] and a variation on second order Møller-Plesset theory [10], both of which should yield reasonable shieldings not only at the high shielding end but also for species that show large and negative shieldings.

In addition to the ab initio shieldings, we have carried out analyses of the sulfur bonding employing the delocalization index of Fradera, Austen, and Bader [11] in the atoms-in-molecules (AIM) approach [12] and also analyze some of the data using the localized orbitals due to Cioslowski [13,14] and the associated covalent bond order [15].

THEORETICAL BACKGROUND

In our discussion we characterize bonds to sulfur by the AIM delocalization index of Fradera, Austen,

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and Bader [11], which for a single determinant wavefunction is identical to the bond order expression of Ángyán, Loos, and Mayer [16]. In addition we occasionally invoke the Cioslowski–Mixon (CM) covalent bond order [15], which, although a noninvariant expression, is very similar to that of Ángyán, Loos, and Mayer. These approaches, which we briefly review here, are intimately related to the concept of the Fermi hole [17,18].

In the closed shell single determinant approach used here the delocalization index may be written as

$$F_{ij} = 2 \sum_{\nu,\mu} \langle \nu \mid \mu \rangle_i \langle \mu \mid \nu \rangle_j \tag{1}$$

Invoking sum rules [19] one obtains

$$\begin{aligned} N = \sum_{i,j} F_{ij} &= \sum_{i,j} \sum_{\nu,\mu} 2 \langle \nu \mid \mu \rangle_i \langle \mu \mid \nu \rangle_j \\ &= \sum_{i,j} \sum_{\mu} 2 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_j \\ &\quad + \sum_{i,j} \sum_{\nu<\mu} 4 \langle \nu \mid \mu \rangle_i \langle \mu \mid \nu \rangle_j \end{aligned} \tag{2}$$

However, the last term in the final expression in Eq. (2) vanishes due to orbital orthogonality, so that we finally get

$$\begin{aligned} N &= \sum_{i,j} \sum_{\mu} 2 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_j \\ &= \sum_{i} \sum_{\mu} 2 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_i \\ &\quad + \sum_{i<j} \sum_{\mu} 4 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_j \end{aligned} \tag{3}$$

The expression for N in Eq. (3) is quite general for single determinant wavefunctions.

Cioslowski and Mixon [15] start with the expressions in Eq. (3), defining the first ($i = j$) term as N_{atomic} and the second ($i < j$) as N_{diatomic}. They then perform an orbital localization procedure which maximizes N_{atomic} while maintaining the first order density matrix constant, a transformation that Cioslowski calls *isopycnic* [13,14]. They then *define* a covalent bond order, $p(i, j)$, between AIM basins i and j in this specific representation as

$$p(i, j) = \sum_{\mu} 4 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_j \tag{4}$$

The more general delocalization index is, as both Fradera et al. [11] and Ángyán et al. [16] point out, invariant to unitary transformations, while the CM bond order definition, in which only the $\mu = v$ "diagonal terms" are kept, is not. However, as Ángyán et al. point out, on the basis of the population-localized orbitals, Cioslowski and Mixon use, the neglected off-diagonal terms are small, and for strictly localizable systems they may be negligible.

The contribution to the CM bond order from molecular orbital μ in the i, j AIM basins is

$$p_{\mu}(i, j) = 4 \langle \mu \mid \mu \rangle_i \langle \mu \mid \mu \rangle_j \tag{5}$$

with the degree of ionicity [20] *defined* as

$$i_{\mu}(i, j) = \frac{\langle \mu \mid \mu \rangle_i - \langle \mu \mid \mu \rangle_j}{\langle \mu \mid \mu \rangle_i + \langle \mu \mid \mu \rangle_j} \tag{6}$$

For simple molecules we can, on the basis of our chemical sense, make a preliminary assignment of covalent bond or lone pair character to the various localized orbitals. In previous work [21] we found this chemical assignment, with a few exceptions, divided the data nicely into two almost disjoint classes, those with i values equal to or greater than 0.88 and those with an i value equal to or less than 0.76. Orbitals in the first class are typed as lone pairs, while those in the latter are classified as covalent bonds (of varying polarity). Our assignment is arbitrary but one we think that is reasonable for our analysis and generally in line with chemical sense. Finally, we define large or significant contributions as those contributing at least 0.04 to the covalent bond order; those with contributions less than this are ignored, although all contributions are contained in the total bond order.

CALCULATIONS

Calculations of absolute chemical shieldings (ppm) were carried out both in a scaled B3LYP [22,23] DFT approach [9] and also our estimated infinite-order Møller-Plesset [10] (EMPI) method employing Gaussian 03 [24]. Gauge-including atomic orbitals [7,25] (GIAO) in a 6-311+G(nd,p) basis were used with six Cartesian d-functions per set and $n = 2$ for sulfur, 1 for all other elements. Geometries were optimized at the B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) levels for the DFT and EMPI shielding calculations, respectively, with frequency calculations confirming the theoretical geometries as energy minima. CM localized orbitals and the associated covalent bond orders were also calculated using the Gaussian 03 suite of programs at the B3LYP/6-311+G(d,p) level, while the electron-localization-function (ELF) code of Noury et al. [26] was used to determine the delocalization indices at the same level of theory.

In NMR shielding calculations of elements of the second long row one typically uses a triple zeta set with at least two sets of d polarization functions on the nucleus of interest. It is practically important to use the smallest basis set possible such that other, larger sets provide no significant change in the calculated shielding. In actuality DFT calculations are relatively so fast that basis set constraints are small, but such is not the case for MP2 or EMPI calculations, especially when large molecules are involved. In the present study we looked at 1, 2, 3, and 5 sets of d-functions on sulfur for OCS where sulfur is rather shielded and for SO_2 where strong deshielding is present. It was confirmed that while small changes do occur in moving from 2 to 3 sets of d-functions, the use of 2 sets provides quite adequate results at the level of theory employed.

Our scaled DFT method [9] results from the discovery that a simple constant rescaling of the paramagnetic contribution can be made such that quantitative predictions are possible. We performed a least squares fit of the DFT paramagnetic contribution, σ_{para}, against the difference of the observed isotropic shielding and the diamagnetic contribution, σ_{dia}, thus deriving a scaling factor, k, for the DFT paramagnetic term. A scaled DFT shielding is then calculated as

$$\sigma_{\text{s, DFT}} = \sigma_{\text{dia}} + k\sigma_{\text{para}} \tag{7}$$

where $\sigma_{\text{s, DFT}}$ is the new estimate of the shielding. The redetermined shieldings are in good agreement with experiment and rival some of the more sophisticated ab initio theoretical approaches. For sulfur we found $k = 0.871(\pm 0.010)$, the value we use in this study.

Our EMPI method [10] uses a particular mixture of RHF and MP2 GIAO approaches. We found that in many cases the Møller-Plesset series of corrections appears to converge in a manner that allows the infinite series to be summed (approximately), so that the EMPI shielding is given by

$$\sigma_{\text{EMPI}} = \sigma_{\text{RHF}} + \frac{2}{3}(\sigma_{\text{MP2}} - \sigma_{\text{RHF}}) \tag{8}$$

A selection of experimental results to compare with theory were taken from the Hinton [1] and Barbarella [2] review articles and the recent study of Aitken et al. [27]. We converted chemical shifts to absolute shieldings using the new sulfur shielding scale of Jackowski, Makulski, and Koźmiński [28] in which *liquid* OCS at 295 K has an absolute shielding of 798.5; these authors also present absolute shieldings for H_2S, CS_2, SF_6, and SO_2. Gas phase values for shielding, such as 817 for OCS, were employed where available.

While both theoretical approaches are initially compared, in our discussion of particular classes of compounds we shall refer only to the scaled DFT results.

DISCUSSION

For convenience of reference all our calculated and the known experimental shieldings are contained in Table 1. Time restrictions prevented EMPI determinations for some of the compounds. In our discussion we shall talk about various subgroups of compounds, but begin in the following section by characterizing the degree of goodness of our calculations by comparing theory and experiment.

Theory and Experiment

Table 1 allows a comparison of experiment results and theoretical calculations for both our DFT and EMPI approaches. Figure 1 illustrates the data graphically. Experimental data were selected so as to be both representative and to cover as wide of range of shielding as possible. Viewing the statistics in Table 2 it is seen that the DFT and EMPI approaches are essentially equivalent whether one characterizes the agreement by the root-mean-square error (RMSE) or the mean absolute error (MAE). The errors expressed as a percentage of the shielding range (of our experimental selection) are of the order of 3%, rather typical for elements in the second long row of the periodic table at this level of theory. So, with an RMSE of 35 ppm one is stating that calculated shieldings are likely correct to within a range of ±70 ppm with 95% certainty. Shielding changes within a group of structurally or electronically related molecules may be significant with differences less than this, but generally speaking shielding changes that differ by 30–50 ppm are not statistically significant. We need to keep this fact in mind when discussing specific results below.

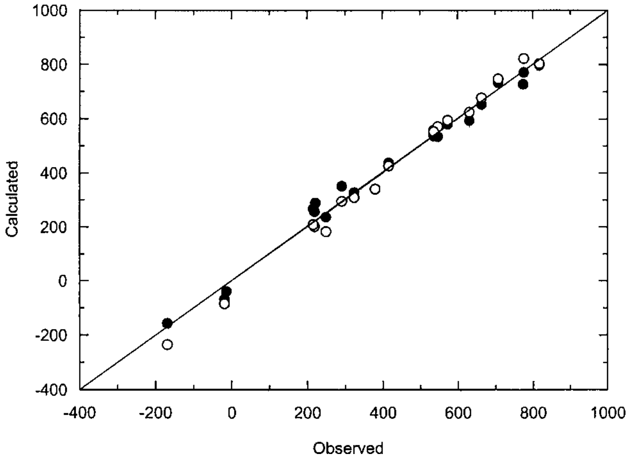


FIGURE 1 Calculated versus observed sulfur absolute shieldings (ppm) for the scaled DFT (solid circles) and EMPI (open circles) methods.

TABLE 1 Observed ^{33}S Chemical Shieldings (Obs) and Those Calculated from the DFT (B3LYP/6-311+G(2d,p)//B3LYP/6-311+G(d,p) Scaled by $k = 0.871$) and EMPI (RHF and MP2/6-311+G(d,p)//MP2/6-311+G(d,p)) Approaches[a]

	DFT	*EMPI*	*Obs*
S^{2-}	1060.1	1059.8	
H_3PS	840.2	917.5	
OCS	797.3	803.2	817
C_2H_4S	771.2	822.2	776
H_2S	733.0	747.3	707.7
C_6H_5NCS	727.3	–	774
F_3PS	717.5	777.5	
$(CH_3)_3PS$	713.0	774.5	
CH_3SH	653.2	677.2	663.0
$(CH_3)_2S$	593.7	624.8	631
CH_3SCN	580.2	595.0	573
HSSH	586.7	638.5	
CS_2	558.4	552.4	536.1
C_6H_5SH	536.9	–	536
Tetrahydrothiophene	534.4	571.5	547
$(CH_3)_2SH+$	528.8	539.6	
$(CH_3)_3SF$	525.7	–	
$(CH_3)_3SBr$	518.3	–	
$(CH_3)_3SCl$	518.1	–	
NNS	512.5	522.0	
3(Exo sulfur)	493.5	575.2	
$(CH_3)_3S+$	483.0	500.9	
8 Br	477.4	–	
8 Cl	475.7	–	
2(Exo sulfur)	470.1	552.6	
8 F	467.3	–	
CH_3SSCH_3	449.2	499.6	
C_2H_4SO	437.6	426.3	416
8	437.4	464.9	
5	387.9	395.9	
7	353.9	–	
$C_2H_4SO_2$	351.7	295.8	291
SF_6	339.9	340.9	379.9
Thiophene	328.5	309.6	324
H_2SO	325.4	300.1	
S^*SS^{-2}	319.8	390.2	
H_2SO_2	314.7	257.0	
Cl_3PS	309.3	448.6	
S_2F_{10}	300.7	–	
CH_3SO_2CCH	295.4	–	
$C_6H_5SHO_2$	290.1	–	222
4	271.2	282.6	
6	268.5	–	
$(CH_3)_2SO_2$	267.7	208.9	216
SS^*S^{2-}	262.7	435.2	
H_2SO_4	259.4	198.4	
$CH_3SO_2C_2H_5$	258.4	200.8	
$(CH_3)_2SO$	257.0	202.0	219
3(Ring sulfur)	250.7	306.2	
Cl_2SO_2	236.7	183.0	249.4
2(Ring sulfur)	234.9	288.6	
Thioformamide	223.7	215.2	
CH_3SO_2CN	211.6	–	
SO_4^{2-}	194.2	126.9	
SO_3	154.3	69.4	
SO_3^{2-}	93.1	10.9	
S_4N_4	85.2	–	
CS	63.1	−2.6	
SF_4	58.9	47.1	
HPS_2 (**1**)	39.5	122.4	
CH_3CH_2SOCl	−39.1	–	−14
Cl_2SO	−67.2	−84.6	−19
SO_2	−157.1	−235.0	−169.7
H_3NSO_2	−157.9	−256.9	
S_2N_2	−174.0	−229.2	
Cl_2S	−291.4	−81.1	
$(CH_3)_2CS$	−322.5	−361.9	
SS^*O	−485.3	−515.1	
H_2CS	−638.9	−646.3	
S^*SO	−687.0	−606.6	
SS^*S	−776.5	−648.7	
SF_2	−908.3	−940.3	
S^*SS	−1437.9	−1272.7	

[a] A set of 2d polarization functions was used on sulfur in both cases.

Singly Bonded Sulfur

Table 3 shows the chemical shieldings and delocalization indices for singly bonded sulfur in a variety of molecules. There is an additive effect as one adds methyl groups to H_2S, yet the CM analysis of the localized orbitals involved indicates that the bond situation is basically the same in the first three cases in Table 3: one nearly pure covalent bond (essentially zero ionicity) and a small (ca. 8%) involvement of one sulfur lone pair. One cannot rationalize the shieldings on the basis of the bonds involved, yet a deshielding of 139 ppm occurs in the sequence.

The cases of Cl_2S and F_2S are quite different. The AIM calculations did not converge for the chlorine case but data are available for the fluorine compound. In Table 4 we see the presence of one polarized ($i = 57\%$) covalent bond and contributions to the CM bond order from four lone pairs, two on fluorine and two on sulfur. In dimethyl sulfide, for example, only one sulfur lone pair contributes 0.0878 (7.8%) to the CM bond order while in F_2S four lone pairs contribute 0.3874 (36.2%).

TABLE 2 Statistics for Calculated Minus Observed Sulfur Chemical Shieldings

	DFT	*EMPI*
Average error	2.6	−6.9
RMSE	33.1	34.9
Percent range[a]	3.4%	3.5%
MAE	27.0	27.8
Percent range	2.7%	2.8%

[a] The range is taken here as the shielding of OCS less that of SO_2, the most shielded and deshielded experimental results available.

TABLE 3 DFT Shieldings (σ, ppm) and Delocalization indices (δ) for some Representative Compounds in Which Sulfur is Singly Bound

	σ	δ
H_2S	733.0	1.10
CH_3SH	653.2	1.13 (SC), 1.07 (SH)
$(CH_3)_2S$	593.7	1.12
HSSH	586.7	1.28 (SS), 1.07 (SH)
Tetrahydrothiophene	534.4	1.06
Cl_2S	−291.4	1.26
F_2S	−908.3	1.05

Sulfides, Sulfoxides, and Sulfones

Table 5 gives results for some representative sulfides, sulfoxides, and sulfones. For these compounds with sulfur bonds to carbon or hydrogen there is a general deshielding as oxygen atoms are added. The case for chlorine, however, is completely different. When one or two oxygen atoms are added to Cl_2S, very strong shielding is observed. This has a parallel in ^{31}P NMR where the addition of oxygen to PCl_3 causes an upfield shift of about 214 ppm. The upfield shifts in the Cl_2S series is likely due to the significant chlorine lone pair backbonding [21] as well as the backbonding of oxygen.

Conventional Multiply Bound Sulfur

Table 6 gives the chemical shieldings and delocalization indices for sulfur in a variety of situations in which it is multiply bound. Table 6a shows examples of conventional double and triple bonds (CS). The R_2CS double bonded species are very deshielded (like their oxygen counterparts) and fall below the CS triply bound molecule, much as ethylene is more deshielded than acetylene in the case of carbon. The results for thiophene and thioformamide which are resonance hybrids are shown in Table 6d and, likely because of their hybrid character, exhibit resonances at higher fields.

TABLE 4 Orbital Populations for Those Dominating the CM Covalent Bond Order in F_2S, the Bond Ionicity (*i*, as a percentage), and the Contribution to the Bond Order (p_{ij})[a]

S	*F*	*i*	p_{ij}	*Type*
0.0190	0.9805	96.2	0.0745	Lone pair (F)
0.0377	0.9533	92.4	0.1438	Lone pair (F)
0.2139	0.7800	57.0	0.6674	Bond
0.9638	0.0181	96.3	0.0698	Lone pair (S)
0.9475	0.0262	94.6	0.0993	Lone pair (S)
			p_{tot} = 1.0716	

[a] The total CM bond order (p_{tot}) is also given and the orbital type is indicated in the last column.

TABLE 5 DFT Shieldings (ppm) for Some Representative Sufides (R_2S), Sulfoxides (R_2SO), and Sulfones (R_2SO_2)

R_2	R_2S	R_2SO	R_2SO_2
C_2H_4	771.2	437.6	351.7
H_2	733.0	325.4	314.7
$(CH_3)_2$	593.7	257.0	267.7
Cl_2	−291.4	−67.2	236.7

The triatomic species are interesting in that the linear species (Table 6b) are characterized quite differently than those which are bent (Table 6c). As well as the usual σ bonds, the linear species may be pictured as having two 3-center-4-electron π bonds. Such bonds are close to being single in character so that the total bond order will be of the order of two which is consistent with the delocalization indices (with the exception of NNS). In the bent triatomics formally there is only one 3-center-4-electron π bond to accompany the two lone pairs on the terminal atoms and the single lone pair on the central atom. The presence of lone pair generally tends to cause deshielding as is observed.

It is worth discussing the S_3 molecule briefly. The terminal sulfur has the lowest calculated shielding of all the molecules we have studied at −1437.9 ppm,

TABLE 6 Sulfur Chemical Shieldings (σ, ppm) and Bond Delocalization Indices (δ) for some Multiply Bound Species

	σ	δ
a. Conventional multiple bonds		
CS	63.1	2.78
$(CH_3)_2CS$	−322.5	1.92
H_2CS	−638.7	2.08
b. Linear triatomics		
OCS	797.3	1.97
C_6H_5NCS[a]	727.3	1.86
SCS	558.4	2.09
NNS	512.5	1.46
c. Bent triatomics		
S^*SS^{2-}	319.8	1.34
SS^*S^{2-}	262.7	–
OSO	−157.1	1.54
SS^*O	−485.3	1.91 (SS) 1.55 (SO)
S^*SO	−687.0	–
SS^*S	−776.5	1.77
S^*SS	−1437.9	–
d. Other systems		
Thiophene	328.5	1.27
Thioformamide	223.7	1.23
SO_3	154.3	1.31
SO_3^{2-}	93.1	1.21

[a] The NCS portion of the molecule is essentially linear.

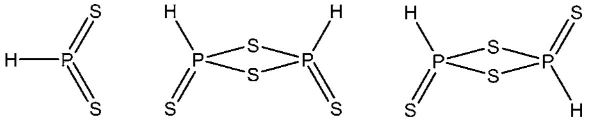
while the central sulfur is also very deshielded at −776.5 ppm. S_3 is the sulfur analogue of ozone, that is, so far as we know, the most deshielded oxygen system. The O_3 experimental shieldings are reported by Gauss and Stanton [29] to be −1290 and −724 ppm for the terminal and central oxygen atoms, respectively. These authors calculate the shieldings using a CCSD(T)/pz3df approach to obtain −1208.2 and −754.6 ppm, in rather good agreement with the experiment. Our scaled DFT efforts [9] for ozone using a scaling factor $k = 0.890$ (ozone data not included in the fit) yielded calculated shieldings of −1375.4 and −926.9; if the ozone data are included in the scaling fit (scale factor $k = 0.827$) values of −1248.5 and −832.9 are obtained. It is not at all surprising that the valence-isoelectronic S_3 molecule has the largest deshielding calculated, and we believe our estimates of this shielding should be reasonably good.

The R_3PS Species; HPS_2 and its Dimers

Just as unusual properties are observed for the phosphine oxides, R_3PO, so, too, would one expect the phosphine sulfides, R_3PS, for which no literature data exist, to behave similarly. The PO or phosphoryl bond in the phosphine oxides is short, of the length of a normal PO double bond, but when one considers its delocalization index relative to a species with a formal double bond (like HPO defined as the normal PO double bond) one obtains a relative bond order of 1.3 [30]. Similar results are obtained for the R_3PS species.

As with the PO cases, one cannot characterize the PS bond in R_3PS simply by its bond length. The Pauling PS single and double covalent bond distances are 1.94 and 2.14 Å, respectively. As Table 7 shows, the bonds in H_2PSH and HPS are of the correct magnitude and can be used to define formal single and double PS bonds. The thiophosphoryl bond length is close to what one would expect for a normal double bond. This is further confirmed by examining the bond lengths for HPS_2 (**1**) and the exo and ring bonds in its dimers **2** and **3** (Scheme 1) shown in Table 8.

Just as in the case of the phosphoryl bond, the proper bond order characterization must be done in terms of the various delocalization indices. The data from Table 7 of the relative delocalization indices indicate that if the PS bond in HPS is defined to be the bond order 2.0, then the bond order of the thiophosphoryl bond is approximately 1.6. That is, it is larger than the corresponding phosphoryl bond but still does not have a formal bond order of two. The larger delocalization index suggests that the thiophosphoryl bond is less polarized than its PO analogue, which is to be expected since the electronegativity difference between P and S is much smaller than that between P and O. This is confirmed by an AIM atom basin population analysis that shows that in moving from the PO to the PS bond the positive charge on the phosphorus atom is reduced by about 0.9 electrons while the negative charge on S is decreased (less negative) by about 0.8 electrons.


1 2 3

SCHEME 1

TABLE 7 Optimized PS Bond Distances (*R*, Å), Absolute Delocalization Indices (δ_{PS}) and Those with Respect to $\delta_{PS}^{rel} \equiv 2.0$ for HPS, and Sulfur Shieldings (σ, ppm) for the R_3PS Species

	R (Å)	δ_{PS}	δ_{PS}^{rel}	σ
a. Reference compounds				
H_2PSH	2.170	1.05	1.13	
HPS	1.951	1.86	(2.0)	
b. R_3PS species				
H_3PS	1.960	1.51	1.62	840.2
$(CH_3)_3PS$	1.972	1.41	1.52	713.0
F_3PS	1.884	1.70	1.83	721.7
Cl_3PS	1.908	1.65	1.77	309.3
$\bar{x}^a$	1.931	1.57	1.68	
s.d.^{a}	±0.036	±0.11	±0.12	

^{a}Statistics are for the R_3PS species.

Krüger et al. [31] have determined the structures and phosphorus NMR shieldings for a number of dithiadiphosphetanes $[RP(S)S]_2$ and dithioxophosphoranes RPS_2, including the cases where R = H that we have studied. Using the IGLO approach [32,33] they find the phosphorus shieldings as given in Table 8. The corresponding sulfur shieldings we calculate are also shown in Table 8 and exhibit significant differences for the exo and ring sulfur atoms.

TABLE 8 PS Bond Distances (R_{PS}, Å), Delocalization Indices (δ_{PS}), and Phosphorus (σ_P) and Sulfur (σ_S) Chemical Shieldings for Compounds **1**, **2**, and **3**

	1	**2** *(Exo)*	**2** *(Ring)*	**3** *(Exo)*	**3** *(Ring)*
R_{PS}	1.925	1.928	2.169	1.930	2.170
δ_{PS}	1.61	1.57	0.90	1.58	0.91
σ_P^a	33	362^b	–	355^b	–
σ_S	39.5	470.1	234.9	493.5	250.7

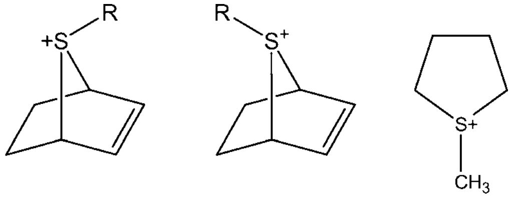
^{a}Ref. [31].

^{b}The phosphorus shieldings are unique for the **2** and **3** compounds.

The similarities in the phosphorus and sulfur shieldings show up in the fact that they are nearly the same for HPS_2 and the average ring shieldings are close to each other. In both cases the HPS_2 shieldings are very much downfield while those of the dimers are in the lower third of the two atoms' shielding ranges.

What is somewhat perplexing is the shieldings of the dimers **2** and **3** in terms of the character of the PS bonds as indicated in Table 8. Pauling's covalent bond radii predict a PS single bond length of 2.14 and a PS double bond length of 1.94, in agreement with the indicated bonds for the structures as drawn. The delocalization indices are also consistent with the calculated bond lengths. The highly deshielded HPS_2 compound can be understood in terms of the isoelectronic SSS molecules whose shieldings are very large and negative. What is not immediately apparent is the fact that one likely would have predicted for the dimers that the exo sulfurs would be further downfield of the ring sulfur atoms, when just the opposite is calculated.

Another example of the similarities between sulfur shieldings and those of related compounds occurs in the 7-thianorbornenes. Interesting shielding differences occur for the syn and anti forms of P-substituted 7-phosphanorbornenes and have been discussed and explained in great detail in earlier work [34] that treated the R = H, CH_3 compounds in the SCF-GIAO approach. One would expect similar results for the RS+ compounds pictured in Scheme 2. The shieldings given in Table 9 are for the two sulfur cases and for the earlier PH and PCH_3 compounds. A comparison of the first with the third and second with the fourth columns, respectively, shows that, indeed, the sulfur analogues of the phosphanorbornenes show nearly the same difference in shielding for the syn and anti cases. The explanation for the relative shifts given earlier [34] for the phosphorus compounds (involving the interaction of the carbon-carbon double bond with the substituent on phosphorus) undoubtedly applies to the sulfur analogues we studied here.



R = H **4** (syn) **5** (anti) **8**

R = CH3 **6** **7**

SCHEME 2 The 7-thianorbornenes.

TABLE 9 Chemical Shieldings (ppm) for the Syn and Anti Thianorbornene Cations **4–7** and the Analogous Phosphanorbornenes, **4′–7′** with P in Place of S+

Syn	**4** 271.2	**6** 268.5	**4′** 269.5	**6′** 266.4
Anti	**5** 387.9	**7** 353.9	**5′** 365.4	**7′** 351.3
Difference	116.7	85.4	95.9	84.9

The S-methyl-tetrahydrothiophenium Cation

Annunziata and Barbarella [35] report a chemical shift for *S*-methyl tetrahydrothiophenium iodide **8I** (as a saturated solution in chloroform, liquid dielectric constant of about five) of 750 ± 50 ppm downfield of CS_2 with a line width of 390 ± 50 ppm. Using the new absolute shielding scale [28] for CS_2 one arrives at an absolute shielding of −214 ppm for this compound. This shielding is currently thought to be the most downfield *observed* shielding of any sulfur compound. Our results, however, and related ones by Bagno [3] cause this assignment to be put in question.

The first part of Table 10 gives our theoretical results for the cation **8** and its fluoride, chloride, and bromide and shows that the shieldings are much, much further upfield of the quoted experimental results. One cannot calculate the iodide with the basis we employ, but using the much smaller (and less reliable) unscaled dft 3-21G approach one obtains shieldings of 481.8 for **8**Br and 475.8 for **8**I which shows that there is no great change from the other halides expected when the iodine anion is involved.

The data for a second model system based on dimethyl sulfide and its methyl sulfonium derivatives given in the second part of Table 10 confirm the fact that formation of the sulfur cation followed by salt formation yields only moderate deshielding effects

TABLE 10 Chemical Shieldings (σ, ppm) for the *S*-methyl tetrahydrothiophenium **8** and Trimethylsulfonium Ions and Their Halides, and Shielding Changes ($\delta\sigma$, ppm) with Respect to Tetrahydrothiophene and Dimethyl Sulfide, Respectively

	σ	$\delta\sigma$
Tetrahydrothiophene	534.4	0.0
8	437.4	−97.0
8F	467.3	−67.1
8Cl	475.7	−58.7
8Br	477.4	−57.0
$(CH_3)_2S$	593.7	0.0
$(CH_3)_2SH+$	528.8	−64.9
$(CH_3)_3S+$	483.0	−110.7
$(CH_3)_3SF$	525.7	−68.0
$(CH_3)_3SCl$	518.1	−75.6
$(CH_3)_3SBr$	518.3	−75.4

relative to the uncharged parent compound. Similar results were obtained by Bagno [3] for $(CH_3)_3S+$, $(CH_3)_3SCl$, H_3S+, and H_3SCl.

The optimized **8**X structures very closely resemble a trigonal bipyramid, the structure expected for sulfur surrounded by five pairs of electrons. The *S*-methyl group and the halide ion take up approximate axial positions, while the ring carbons adjacent to sulfur and the sulfur lone pair are basically in equatorial positions. The picture suggested is that of an *S*-methyl tetrahydrothiophenium cation interacting with a halide anion. The AIM net charge on sulfur is on average +0.42 while that for the halide is approximately −0.77, clearly indicative of a salt with little or no covalent interaction between sulfur and the halide. This is further borne out by the large sulfur-halide distances of 2.152 (F), 2.872 (Cl), and 3.052 (Br) compared to the Pauling covalent distances of 1.68, 2.03, and 2.18, respectively. The calculated changes in the sulfur-halide distance is reflective of the relative size of the anions.

In the various cases the formation of the halide complexes leads to a deshielding of about 70 ppm relative to the parent compound; the shielding changes for the isolated sulfur cations is 30–40 ppm larger than this. The experimental line width of *S*-methyl thiophenium iodide is very large (390 ± 50 ppm), but it is difficult to think that the theoretical and experimental shieldings could differ by nearly 700 ppm. We believe the quoted experimental result to be in error, a judgment also rendered by Bagno [3].

An additional argument can be made from methylation effects. The hydrides of both elements (H_2S and PH_3) have experimental shieldings [36] that are near the extremes of shielding for S and P compounds (707.7 and 594.4 ppm, respectively). Replacement of one H by methyl causes deshielding in both hydrides (to 663.0 for MeSH, and 491.9 for $MePH_2$). Replacement of a second H causes further deshielding: Me_2S, 631; Me_2PH, 427. In the P series, a third replacement is possible, and further deshielding occurs: Me_3P, 391.7. Notice that the magnitudes of the deshielding on each methylation step are similar.

Further methylation gives onium salts of both elements. The shift for $Me_4P^+I^-$ is 303.3 [37], and thus the trend of deshielding is continued, by an amount not unlike that seen on replacement of H by methyl. The experimental values for Me_3S^+ compounds are not known, but it seems that a downfield shift of rather similar magnitude would be found. Therefore, a calculated value of 518.3 for $Me_3S^+Br^-$ seems perfectly reasonable; here a deshielding of 113 ppm from Me_2S occurs, to be compared to 88.6 ppm on methylation of Me_3P.

If 483.0 is accepted as being, within limits, the correct value for Me_3S^+, then there is no reason to believe that a shielding of −214 as reported for the methiodide of *S*-methyl tetrahydrothiophene would be possible. We believe this value to be incorrect.

SUMMARY

Calculations in the correlation-including scaled DFT and EMPI approaches provide chemical shieldings for sulfur that span the range of sulfur shieldings and show agreement with experiment of about 3% of the shielding range. The atoms-in-molecules delocalization index and a covalent bond order from specific localized orbitals in the DFT approach have been used to characterize sulfur's bonding and to relate it, where possible, to the calculated shieldings.

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