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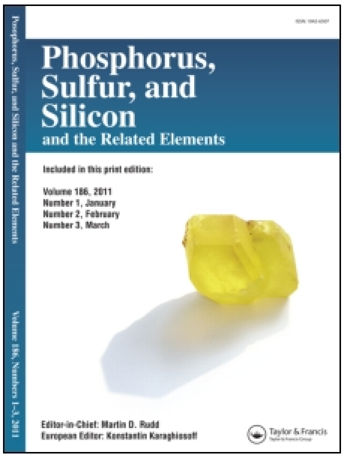

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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To cite this Article Fleischer, Ulrich(1999) 'Calculations of Phosphorus Nuclear Magnetic Shielding Tensors - Studies on Phosphorus Chalcogen Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 663 — 666

To link to this Article: DOI: 10.1080/10426509908546332

URL: http://dx.doi.org/10.1080/10426509908546332

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Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 663-666
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Printed in Malaysia

Calculations of Phosphorus Nuclear Magnetic Shielding Tensors – Studies on Phosphorus Chalcogen Compounds

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Keywords: Nuclear Magnetic Shielding Tensors; Chemical Shift Tensors; IGLO; GIAO; Phosphorus-Chalcogen Compounds

The nuclear magnetic shieldings (or the NMR chemical shifts) are sensitive probes of the local electronic structure. The shielding tensors, their principal values and their principal axes system, give even more insight into the electronic structure, since they reflect the different interactions between occupied and unoccupied orbitals induced by a magnetic field oriented along the different axes.

Results of IGLO calculations[1] and experimental data for the principal values of the phosphorus shielding tensors, $\sigma_{ii}(P)$, within the series of $P_4O_6Z_n$ molecules[2] (Z=O, S and Se, n=0...4) are compared in Figure 1. They agree very well, the average deviation is about 21 ppm. Even better agreement can be achieved if one determines two straight lines (with slope 1), one for σ_{33}, the most shielded principal value, and one for σ_{11} and σ_{22}. The intercept of the latter is some 30 ppm smaller and closer to the ideal value, 328 ppm, the shielding of the reference system. As normally found for saturated systems not having low-lying excited states (low-lying virtual orbitals) correlation effects are comparably small in these molecules. MP2-GIAO calculations[3] on the model system $ZP(OH)_3$ differ only slightly from the corresponding GIAO calculations. DFT calculations on $ZP(OH)_3$ and ZP_4O_6 do not give any hint to large correlation effects either. They seem to be a little bit off the Hartree-Fock and the MP2 data, though.

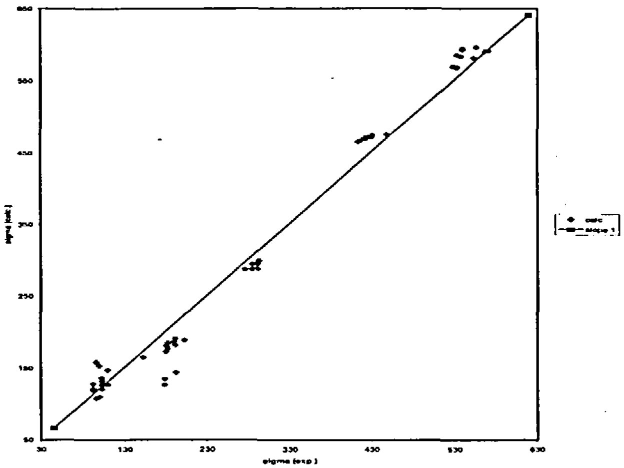

FIGURE 1 Principal values of the phosphorus shieldings, $\sigma_{ii}(P)$, in $P_4O_6Z_n$

The principal values of $\sigma(P)$ within the ZP_4O_6 series are documented in Table 1. To discuss the trends observed qualitatively we recall that the shielding is given as a sum of two (or – depending on the method used – several) terms.

TABLE 1 MO contributions to $\sigma_\parallel$ and $\sigma_\perp$ for the substituted phosphorus [a)]

	P_4O_6		OP_4O_6		SP_4O_6		SeP_4O_6	
	$\sigma_\parallel$	$\sigma_\perp$	$\sigma_\parallel$	$\sigma_\perp$	$\sigma_\parallel$	$\sigma_\perp$	$\sigma_\parallel$	$\sigma_\perp$
σ	480	129	596	299	585	189	568	144
ZP	19	-385	94	-301	100	-401	90	-432
PO	-121	-84	-113	-73	-118	-75	-120	-77

[a)] in ppm; $\sigma_{22} = \sigma_{11}$ because of the (local) C_{3v} symmetry; ZP – lone pair contribution for P_4O_6, sum of PZ bond and Z lone pairs for ZP_4O_6

A qualitative discussion one can be limited to the so-called paramagnetic contribution, σ^P. It can be expressed by the matrix elements of the first order perturbation operators and the energy difference between the occupied orbitals i and the unoccupied or virtual orbitals a. The perturbation operators are of (local) angular momentum type.

$$\sigma_i^p \sim \langle i|\hat{l}_i|a\rangle \cdot \langle i|\hat{l}_\mu r_\mu^{-3}|a\rangle \cdot (E_a - E_i)^{-1}$$
$$l_a = (r - R_a) \times \hat{p}$$

The perpendicular component of the ZP contribution is the most deshielding one. A magnetic field perpendicular to the bond induces interactions with low-lying virtual orbitals (e.g. σ^*(PO)). Since it is this bond which is formally replaced when going from one molecule to the other, it is this component that changes the most in the series. The parallel component is shielding, no deshielding interaction can be induced by a field along the bond direction. The increase of the shielding going from P_4O_6 to the other members of the series is typically found for systems having a cylindrical charge density along an axis.

Grossmann, Potrzebowski and coworkers recently performed solid state NMR studies on ^{71}Se enriched $SeP(CH_3)_3$ and $SeP(C_6H_5)_3$[4]. Experimental and calculated data are compared in Table 2. As found for other saturated phosphorus compounds theoretical and experimental data agree well.

TABLE 2 Principal values of σ in $SeP(CH_3)_3$ and $SeP(C_6H_5)_3$ [a]

	$SeP(CH_3)_3$			$SeP(C_6H_5)_3$ [b]					
	σ_{33}	σ_{22}	σ_{11}	σ_{33}	σ_{22}	σ_{11}	σ_{33}	σ_{22}	σ_{11}
Exp.	367	287	277	376	267	224	376	267	224
Calc.	407	272	267	396	239	219	397	245	216
[c]	381	286	285						

[a] in ppm; see [4] for further details

[b] two molecules in the unit cell, only one spectrum observed experimentally

[c] data for the central molecule of a $(SeP(CH_3)_3)_6$ cluster

As pointed out above, larger deviations are observed for σ_{33}. Correlation effects can most probably be excluded as an explanation since MP2-GIAO calculations (for the C_{3v} optimized structure) give only slightly different principal values than the corresponding GIAO calculations (σ_{33} even increases). The results of a calculation on a $(SeP(CH_3)_3)_6$ cluster modeling the crystal environment might be taken as an indication that intermolecular interactions are the reason for the larger deviations observed for σ_{33}. Further studies have to be done to check this explanation.

For low coordinate phosphorus the deshielding interactions induced by the magnetic field are distinctly larger than for the compounds discussed above. Therefore correlation effects become more important. As can be seen from Table 3 the shieldings calculated for PS_3^- at the Hartree-Fock level converge to about –110 ppm. Inclusion of correlation effects at the MP2 level leads to a value of about 20 ppm, which is in nice agreement with recent experimental data of Karaghiosoff and Schuster[6].

TABLE 3 Isotropic shieldings of PS_3^- [a]

IGLO		GIAO			Experiment
Basis	HF	Basis	HF	MP2	
II	-93	DZP	-130	24	
III	-108	TZ2P	-114	17	31 [b] 276 [c]

[a] in ppm
[b] Karaghiosoff et al., ref [5]
[c] Roesky et al., ref. [6]

PSe_3^- is calculated to be about 70 ppm more deshielded than PSe_3^- at the MP2 level (200 ppm at Hartree-Fock level). This is in contradiction to the experimental findings which give PSe_3^- more shielded than PS_3^- by 85 ppm[6]. Preliminary calculations of the spin-orbit corrections using the SOS-DFT package[7] give only a minor correction for PS_3^- but about 160 ppm for PSe_3^-. Correlation and spin-orbit effects have to be taken into account for PSe_3^-, as found recently for the valence-isoelectronic CBr_3^+ [8].

Acknowledgements
The author thanks W. Kutzelnigg (Bochum) and P. Pulay (Fayetteville) for their support. He thanks J. Gauss as well as O.L. Malkina and V.G. Malkin for a copy of their programs. Financial support by 'Deutsche Forschungsgemeinschaft', 'Fonds der Chemischen Industrie' and 'National Science Foundation' (grant no. CHE-9707202) is gratefully acknowledged.

References

[1] W. Kutzelnigg, U. Fleischer and M. Schindler, *NMR Basic Princ. Prog.*, **23**, 165 (1990).

[2] U. Fleischer, F. Frick, A.R. Grimmer, W. Hoffbauer, M. Jansen and W. Kutzelnigg, *Z. anorg. allg. Chem.*, **621**, 2012 (1995).

[3] J. Gauss, *J. Chem. Phys.*, **99**, 3629 (1993).

[4] G. Grossmann, M.J. Potrzebowski, U. Fleischer, K. Krüger, O.L. Malkina and W. Ciesielski, *Solid State Nucl. Magn. Reson.*, in press.

[5] K. Karaghiosoff and M. Schuster, 4. Workshop "NMR-Spektroskopie an Phosphorverbindungen", Chorin, 1997.

[6] H.W. Roesky, R. Ahlrichs and S. Brode, *Angew. Chem.*, **98**, 91 (1986).

[7] V.G. Malkin, O.L. Malkina and D.R. Salahub, *Chem. Phys. Lett.*, **261**, 335 (1996).

[8] M. Kaupp, O.L. Malkina, and V.G. Malkin, *Chem. Phys. Lett.*, **265**, 55 (1997).