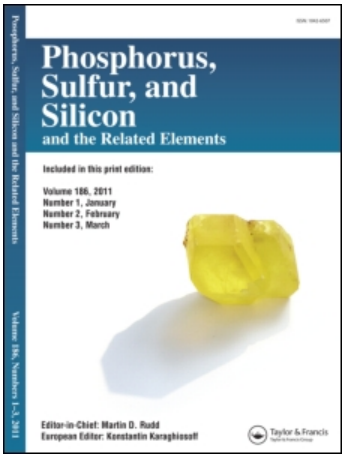

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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U. Fleischer[a]; K. Krüger[b]; G. Grossmann[b]; W. Kutzelnigg[a]
[a] Lehrstuhl für theoretische Chemie, Ruhr-Universität Bochum, BOCHUM, RFA [b] Institut für Analytische Chemie, Technische Universität Dresden, Dresden, RFA

To cite this Article Fleischer, U. , Krüger, K. , Grossmann, G. and Kutzelnigg, W.(1994) 'Nuclear Magnetic Shielding Tensors in Phosphorus Containing Ring Systems. A Theoretical Study', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 217 — 220
To link to this Article: DOI: 10.1080/10426509408021820
URL: http://dx.doi.org/10.1080/10426509408021820

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 217-220
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NUCLEAR MAGNETIC SHIELDING TENSORS IN PHOSPHORUS CONTAINING RING SYSTEMS. A THEORETICAL STUDY

U. FLEISCHER [a], K. KRÜGER [b], G. GROSSMANN [b], W. KUTZELNIGG [a]

a Lehrstuhl für theoretische Chemie, Ruhr-Universität Bochum
D-44780 BOCHUM, RFA

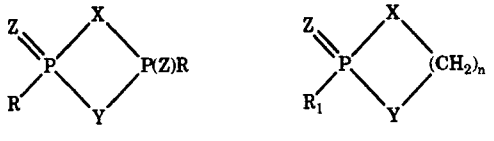
b Institut für Analytische Chemie, Technische Universität Dresden
Mommsenstr. 13, D-01062 Dresden, RFA

The nuclear magnetic shieldings (or the NMR chemical shifts) are a quite sensitive probe of the local electronic structure in a given system. The shielding tensors, their principal values and their principal axes systems, give even more insight into the electronic structure, since they reflect the different interactions between occupied and virtual orbital induced by different field directions.

In comparison to the huge amount of data for isotropic shieldings quite a small number of data for the principal values have been reported. Even less information is available for the orientation of the principal axes systems. Calculations of the shielding tensor which directly furnish these data can be used as a source of interesting, complementary information.

We here report on IGLO calculations of phosphorus containing ring systems. The IGLO-method[1] (IGLO stands for **I**ndividual **G**auge for **L**ocalized **O**rbitals) is a coupled Hartree-Fock (CHF) type method for the calculation of NMR shielding tensors and the magnetic susceptibilities of (closed shell) molecules. At variance with traditional CHF, individual gauge origins are used for different localized MOs. One thus avoids the problem of imperfect cancellation of spurious dia- and paramagnetic contributions and gets reliable results for a wide range of classes compounds with small or medium sized basis sets[2].

We have studied the following oxo- and thiophosphetanes and -phospholanes



where R=H, CH_3, C_6H_5, SCH_3; R_1=H, CH_3, NH_2, OH, F ; X, Y, Z=O, S and n=1, 2.

The calculated principal values compare well with their experimental counterparts (see figure 1). This is also true for the orientation of the principal axes. An IGLO cal-

culation on $CH_3SP(S)SSP(S)SCH_3$ yields 107° as angle between the direction of σ_{33} and the PP axis[3] (see figure 2). This is in good agreement with the experimental value[3] of 105°. For RP(S)SSP(S)R the calculated data[4] - R=C_6H_5 - (111°) can be compared to the experimental ones[5] with R=p-$CH_3OC_6H_4$ (114°).

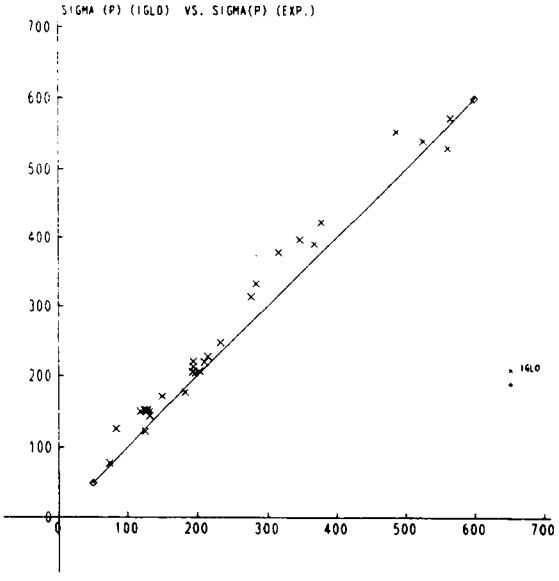


FIGURE 1 Calculated principal values of the shielding tensors vs. experimental ones. The straight line represents the ideal behaviour, i.e. it has slope 1 and goes through the origin.

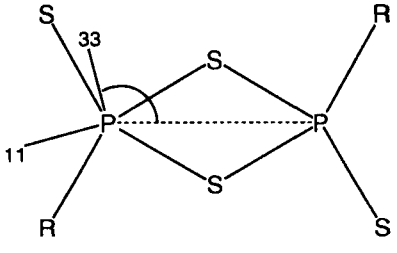


FIGURE 2 Orientaion of the principal axes. The principal axes corresponding to σ_{22} is not shown, it is perpendicular to the mirror plane.

The calculated data can be used for the assignment of the principal axes, this information is not available from a routine solid state NMR experiment. One can also do systematic studies, i.e. look at substituent effects or the effect of the exchange of sulfur by oxygen (or vice versa).

If one of the ring sulfur atoms in $CH_3P(S)SSP(S)CH_3$ is replaced by an oxygen atom the principal values of the phosphorus shielding tensor change to a different extent (see

table I). Larger changes are found for σ_{11} and σ_{33} , the effect on σ_{22} is comparably small (for all principal values the exchange of sulfur by oxygen results in a decreased shielding). The same trends have also been observed experimentally for the triisopropylphenyl substituted systems[6].

TABLE I MO contributions to σ_{ii} [a)]

MO	$CH_3P(S)SSP(S)CH_3$			$CH_3P(S)SOP(S)CH_3$		
	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}
σ	152	228	554	79	207	489
P=S	−346	−262	98	−423	−281	101
P-S	−54	−53	−119	−40	−77	−157
P-O				−82	−34	−107
P-C	−154	−151	−114	−154	−167	−151
R	780	746	807	776	766	802

a) in ppm; P=S - sum of PS bond and lone pair S orbitals; R - sum all orbitals not explicitely given

We can analyze these observations a little further. Within the IGLO approach the shielding tensors are calculated as sums of contributions of localized MOs. These show a different behaviour for each of the principal values (see table I). Most of the change of σ_{11} is found in the P=S contribution, whereas for σ_{33} the P-S and the P-C contribution change the most.

For an analysis we recall that the shielding is given as a sum of two (or within the IGLO scheme of three) terms. For a qualitative discussion we can concentrate on the paramagnetic term. This is expressible in matrix elements of the first order perturbation operators and the energy difference between the occupied oritals i and the unoccupied or vitual orbitals a. The perturbation operator, $\hat{l}_o$, is of (local) angular momentum type.

$$\sigma^{pp}{}_i \sim < i \mid \hat{l}_i \mid a > < i \mid \hat{l}_\mu / r_\mu^3 \mid a > (E_a - E_i)^{-1}$$

$$\hat{l}_o = (r - R_o) \times \hat{p}$$

In principle all virtual orbitals should be taken into account. This would, of course, make a qualitative analysis impractible. In favourable cases, however, one can restrict the analysis to one or a few virtual orbitals. For the systems compared here - as a first approximation - two PS σ^*-orbitals are replaced by PO σ^*-orbitals. The different behaviour of the MO-contributions for the different principal values results from the fact that an interaction of occupied and virtual orbitals can only be induced if those and the magnetic field are orthogonal to each other (the perturbation operators are of angular momentum type). The P=S contribution to σ_{33}, e.g., changes only very slightly, since this direction is more or less parallel to the PS bond and thus no interaction with the PO σ^*-orbitals can be induced.

The exchange of an exo P(S) by a P(O) bond can be studied along the same lines. Going from $CH_3P(S)OOP(S)CH_3$ (σ_{33}, σ_{22}, σ_{11}: 484, 192, 42ppm) to $CH_3P(O)OOP(O)CH_3$ (σ_{33}, σ_{22}, σ_{11}: 520, 239, 207ppm) results in large changes in σ_{11}. The principal values are more shielded in the P(O) compound. It is interessting to note that comparable effects are observed in going from P_4O_6S to P_4O_7[7]. As for the phosphetanes in these compunds an exo P(S) bond is replaced by a P(O) bond in a ring system with PO bonds. The substituted P_4O_6 systems have a higher symmetry (C_{3v}) and thus only two different principal values, $\sigma_{\parallel}$ and $\sigma_{\perp}$, occur (563, 194ppm for P_4O_6S and 576, 295ppm for P_4O_7). The difference between the P(S) and P(O) compound is more or less due to only one MO contribution, namely the P(Z) contribution to $\sigma_{\perp}$, which changes by about 100ppm.

Acknowledgements

We thank M. Schindler, U. Meier, C. van Wüllen for their work on parts of different versions of the IGLO programme and for helpful comments, R. Franke, V. Staemmler, G. Ohms, H. Beckmann and K. Eichele for fruitful discussions. G. Ohms, H. Beckmann and M. Bühl provided data prior to publication. Some of the calculations were done on the CYBER 205 of 'RZ der Ruhr-Universität Bochum', on the CRAY YMP of 'HLRZ der KFA Jülich' and on the SNI 600 of 'RZ der RWTH Aachen'. Financial support by Deutsche Forschungsgemeinschaft und Fonds der chemischen Industrie is gratefully acknowledged.

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