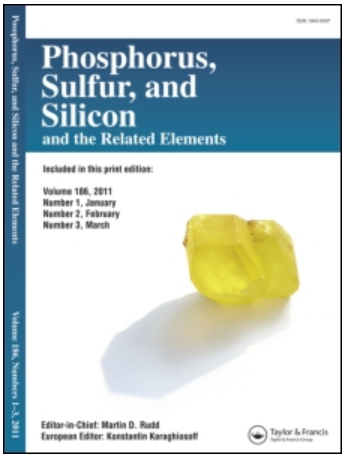

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IGLO Calculations of NMR Chemical Shifts in Some Silicon and Phosphorus Containing Polycycles

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IGLO CALCULATIONS OF NMR CHEMICAL SHIFTS IN SOME SILICON AND PHOSPHORUS CONTAINING POLYCYCLES

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NMR is one of the spectroscopies most widely used by chemists. The dependence of the NMR chemical shifts on the local (electronic) structure make them a powerful tool for the identification of compounds as well as for structure elucidation. Additionally the chemical shifts can be taken as a probe for the electronic structure in the neighbourhood of the nucleus studied. More information can be gained if not only the isotropic values of the chemical shifts (or the nuclear magnetic shieldings) but the full tensors (i.e. the principal values and the orientation of the principal axes system) are available.

We here report on IGLO calculations of silicon and phosphorus NMR chemical shifts (nuclear magnetic shielding tensors) in polycyclic systems of tetrahedrane, prismane, and cubane type (X=P, SiR, CR).

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. It has been applied to a wide range of compounds and yields reliable results with small or medium sized basis sets[2]. For Si, e.g., we found 8 and 21ppm as mean and maximum deviation between calculated and experimental data.

TABLE I Comparison of calculated and experimental data [a)]

	δ(Si, P)		δ(C, Si)	
	IGLO	exp.	IGLO	exp.
P_4	-545	-553 (gas phase value)		
Si_4R_4	-189 (R=H)			
	-244 (R=SiH_3)	39 (R=Si(t-But)$_3$)		
[b)]	-90 (R=SiH_3)	53 (R=Si(t-But)$_3$)		
Si_6R_6	-86 (R=H)	-22 (R=2,6-di-i-PropPh)		
Si_8R_8	-41 (R=H)	0 (R=2,6-di-i-PropPh)		
$P_4C_4R_4$	235 (R=H)	257 (R=t-But)	-12 (R=H)	-29 (R=t-But)
$P_4Si_4R_4$	-182 (R=H)	-177 (R=t-But)	-15 (R=H)	-29 (R=t-But)

a) chemical shifts in ppm; δ(P) with respect to 85% H_3PO_4, δ(C) and δ(Si) with respect to TMS; experimental data from ref. 3

b) Si-atoms of the silyl groups

The calculated NMR chemical shifts compare well with the experimental ones. The large difference of δ_P in $C_4R_4P_4$ and $P_4Si_4R_4$ is well reproduced. Large deviations, however, occur between theoretical and experimental data for Si_4R_4. But since the chemical shifts of silyl substituted silanes are at much lower frequencies (e.g. δ_{Si} for $H\underline{Si}(SiMe_3)_3$ −115 and −136 for $\underline{Si}(SiMe_3)_4$), a reconsideration of the experimental data may be recommended.

TABLE II Principal values of shielding tensors

	X_2H_4	$X_4(T_d)$	$X_6(D_{3h})$	$X_8(O_h)$	X_2H_4	$X_4(T_d)$	$X_6(D_{3h})$	$X_8(O_h)$
	X = P				X = N			
σ_{33}	593.3	1025.6	731.6	388.7	254.3	317.7	259.0	−13.9
σ_{22}	574.9	1025.6	293.3	361.8	184.7	317.7	2.4	−51.8
σ_{11}	496.1	592.9	250.7	361.8	176.3	130.0	−99.3	−51.8
σ	554.8	881.4	425.2	370.7	205.1	255.1	53.7	−39.1
	X = SiH				X = CH			
σ_{33}	503.9	674.2	656.8	467.5	194.6	243.9	231.4	168.5
σ_{22}	481.3	674.2	372.7	467.5	180.6	243.9	144.6	168.5
σ_{11}	481.3	344.1	354.2	313.5	180.6	192.3	138.1	128.0
σ	488.9	564.2	461.3	416.2	185.3	226.7	171.4	155.0

a) in ppm; principal values: σ_{33}, σ_{22} and σ_{11}

All systems with three membered rings have (at least) one distinctly shielded principal value. This is in agreement with the trends found experimentally, e.g. for hydrocarbon rings[4].

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