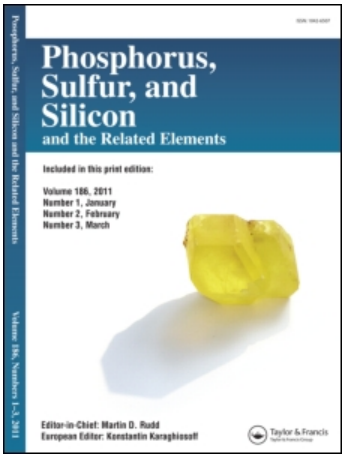

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IGLO Calculations of Phosphorus NMR Chemical Shifts

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IGLO CALCULATIONS OF PHOSPHORUS NMR CHEMICAL SHIFTS

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The IGLO-method[1] (IGLO stands for Individual Gauge for Localized Orbitals) 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 compounds using small or medium sized basis sets[2].

In addition, the IGLO-method permits a direct analysis of the results because it yields the chemical shifts and the susceptibilities as sums of contributions of localized orbitals.

The calculations directly furnish the principal axis system and the principal values of the shielding tensors of all nuclei of the molecule.

For a wide range of phosphorus compounds, i.e., a shift range of roughly 1000ppm, the mean deviation of theoretical and experimental data is some 20 to 30ppm (see figure 1).

Deviations for strongly deshielded nuclei are normally larger than those found for shielded ones, since theory at this level has a tendency to overestimate the deshielding contributions.

Additionally one has to keep in mind that the systems studied theoretically and experimentally differ from each other. A calculation is performed for an isolated molecule with fixed nuclei, whereas most of the experimental data are measured in solution or condensed phase at room temperature.

The effect of errors or uncertainties of the geometries used can be estimated from the calulated dependences of the shielding on the internal coordinates to be of the order of some 10ppm.

For methylenephosphane, e.g., two experimentally determined structures are known from independent microwave studies. The calculated shielding for both structures, which differ by about 0.1kcal/mol in energy, differs by 8ppm.

For unsaturated phosphorus-carbon compounds, e.g., phosphaalkynes, -alkenes, -benzenes, -cyclopentadienylanions, the calculated chemical shifts compare well with the experimental data (e.g., table I). Larger deviations occur for the more deshielded systems, e.g., phospacyclopentadienyl systems with a phosphorus-phosphorus bond.

The shielding tensors of 2,4,6-t-$Bu_3C_6H_2P{=}C(SiMe_3)_2$ and 2,4,6-t-$Bu_3C_6H_2C{\equiv}P$ are known from solid state experiments[3]. The calculated data, i.e., the principal values and the principal axis systems, for compounds with smaller substituents (e.g., C_6H_5, SiH_3) are found to agree well with the corresponding experimental data (e.g., table II).

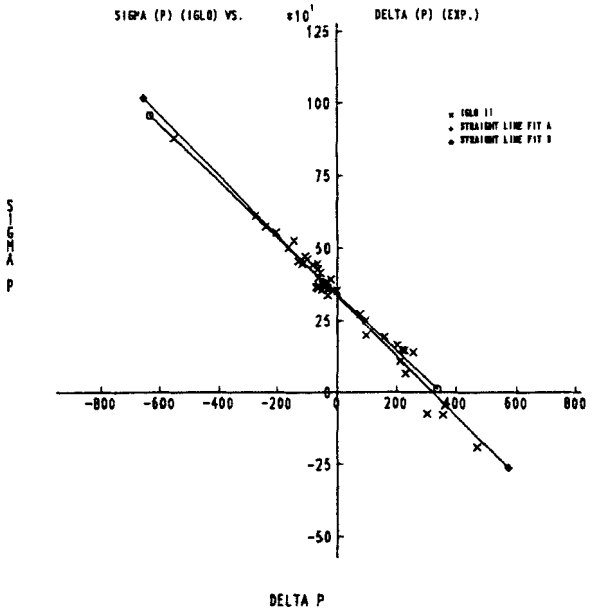

FIGURE 1 Theoretical shieldings vs. experimental shifts. The straight line fit A (the data of the more deshielded systems excluded) yields a slope of -0.98 ± 0.03 with 26.5 as mean deviation, the straight line fit B -1.05 ± 0.03 and 32.4.

TABLE I Phosphorus chemical shifts [a]

molecule	IGLO	exp.	ref.	molecule		IGLO	exp.	ref.
CH_2PH	269	231	4	P_5^-		528	470.2	7
CH_2PPh	338			P_4CH^-	P_1	382	362.1	7
CH_2PPh	336				P_2	414	355.1	7
CH_2PPh'	333			$1,2,3\text{-}P_3(CH)_2^-$	P_1	274	262.9	8
CH_2PAr		290	4		P_2	343	273.1	8
CH_2PCl	341	300.4	5	$1,2,4\text{-}P_3(CH)_2^-$	P_1	283	239.0	9[b]
CF_2PH	−62	−62	4		P_4	252	252.2	9[b]
Phosphabenzene	227	211	6	$1,2\text{-}P_2(CH)_3^-$		195		
				$1,3\text{-}P_2(CH)_3^-$		150	187.6	10[b]
$c\text{-}C_2H_2P^+$	340			$P(CH)_4^-$		63.2	77	11
Triphosphabenzene	294			$PH(CH)_4$		−39.7	−49.2	11

a) w.r.t. 85% H_3PO_4; PH_3 was used as a primary reference with $\delta(PH_3) = -240$ppm; the shielding $\sigma_P(PH_3)$ is 575.5
Ph = Phenyl · Ph'= 2,6-Dimethylphenyl · Ar = 2,4,6-Tri-tert-butylphenyl
b) data of tert-butyl substituted species

The orientation of the principal axes of the shielding tensors can be rationalized qualitatively. The shielding is given as a sum of two (or within the IGLO scheme of three) terms. For a qualitative analysis one can concentrate on the paramagnetic contribution. This is expressible in terms of the 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 is of (local) angular momentum type.

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

In principle all virtual orbitals should be taken into account. This would, of course, make a qualitative analysis impractible. In favorable cases, however, one can restrict the analysis to one or a few virtual orbitals. Favorable cases in this sense are systems where there is a dominating induced interaction, e.g., with a low lying π^*-orbital. Since the magnetic field and the interacting orbitals have to be orthogonal to each other (the perturbation operators are of angular momentum type), the orientation of the most deshielded principal axis can be estimated quite easily for each MO. For the methylenephosphanes the most deshielded axis is always in the plane perpendicular to the bonds or the lone pair. Since the lone pair is higher in energy and localized closer to the nuclei, its contribution will be more important than those of the other MOs.

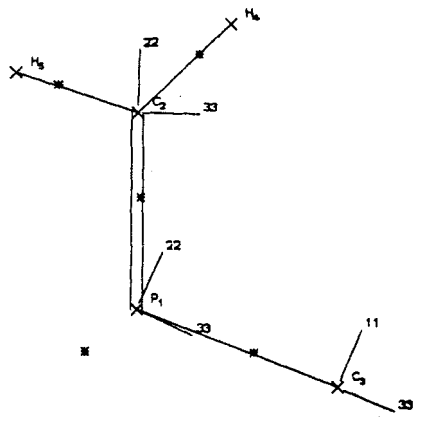

FIGURE 2 Orientation of the principal axes of σ_P and σ_C in $C_6H_5P{=}CH_2$, only the C_α of the ring is shown. The asterisks mark the centroids of charge of the localized MOs.

TABLE II Principal values of phosphorus chemical shifts [a]

molecule	δ_{33}	δ_{22}	δ_{11}	δ		δ_{33}	δ_{22}	δ_{11}	δ
HCP	−684	310	310	−32	CH_2PH	−156	140	824	269
PhCP	−411	172	229	−3	$CH_2PH_2^+$	−142	−45	421	78
PhCP	−399	158	215	−9	CH_2PH_3	−224	−61	−49	−111
Ph'CP	−317	158	247	29	CH_2PH_3	−239	−71	−32	−113
					$CH_3PH_3^+$	−157	−79	−79	−105
ArCP [b]	−274	140	229	31					

a) w.r.t. 85% H_3PO_4; PH_3 was used as a primary reference with $\delta(PH_3) = -240$ppm; the shielding $\sigma_P(PH_3)$ is 575.5
Ph = Phenyl · Ph'= 2,6-Dimethylphenyl · Ar = 2,4,6-Tri-tert-butylphenyl
b) experimental data; ref. 3

The trends found for the phosphorus shielding tensors and the MO contributions ($\sigma_{\|}$, $\sigma_{\perp}$) in YPF_3 compounds (Y = 'lone pair', H^+, CH_3^+, O, S) can be discussed along the same lines. In these cases the most important deshielding interactions are those with the low lying virtual orbitals of σ^*-type, i.e., the PF antibonding orbitals. The PF contributions are more or less transferable within the series, becoming a little larger for the positively charged species where the virtual MOs are lower in energy and are more compact. Distinct changes occur for the YP contribution. The parallel component is quite small and nearly the same for the systems where the bond has purely σ-character. For Y=O and S it is much larger, a typical effect of a cylindrical charge distribution with the external field parallel to cylinder axis. The perperdicular component, the most deshielded one in these systems – it is this field direction which induces the interaction with the σ^*-orbitals – shows the largest changes. Going from a lone pair to a PH or PC bond, the energy of the MO decreases and the MO is

localized away from the nucleus resulting in smaller deshielding. The situation is not that clearcut for Y=O and S. Although the same argument holds in principle – which can be seen for Y=O –, the additional π-type bonds seem to overcompensate the effect for Y=S.

It is interesting to compare the shielding tensors of the double bonded systems CH_2PH and $CH_2PH_2^+$ to those of CH_2PH_3 (table II). The striking difference between the semipolar double bonded and the double bonded system is the lack of a distinctly deshielding principal value for the former system which is more similar to the phosphonium system, $CH_3PH_3^+$. The difference of the most deshielded principal value between CH_2PH and $CH_2PH_2^+$ is in line with the findings that the lone pair contributions are the most deshielding ones.

The examples discussed here show that IGLO calculations furnish an interesting and useful source of information not always available from experiments.

They can be used as a means of an analysis of the spectra and help to solve problems of structure determination. Systematic studies of classes of compounds, substituents effects and geometry dependences are possible. Since the full shielding tensor is calulated, the principal values and axes are always availiable. The MO-contributions can be analyzed and thus yield a (qualitative) interpretation of the observed trends.

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