ABSOLUTE SHIELDING SCALE FOR ^{31}P FROM GAS-PHASE NMR STUDIES

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Differences in the ^{31}P nuclear shielding in the zero-pressure limit have been measured in seven compounds. An absolute ^{31}P shielding scale based on the PH_3 molecular beam data is established and the absolute shielding of the standard liquid reference (85% aqueous H_3PO_4) is found to be 328.35 ppm, based on PH_3 being 594.45 ± 0.63 ppm. Comparisons with ab initio calculations show that calculations using local origins (the IGLO method) are in good agreement with experiment.

1. Introduction

Ab initio theoretical calculations of shielding of nuclei in the second row of the periodic table, especially ^{29}Si, ^{31}P, ^{33}S, have recently become available [1–5]. Comparisons of the chemical shifts between different nuclear environments are routinely measured by NMR spectroscopy in solution or neat liquids. The theoretical calculations are for the isolated molecule at its equilibrium structure. Proper comparisons with experiment require that the experimental data be free of intermolecular effects and be expressed in absolute terms (the calculated values) rather than as differences between absolute shielding. This requires using as a primary standard one molecule in which the absolute shielding is known independently of NMR measurements. There are the further theoretical corrections for rovibrational averaging which are essential in converting the frozen equilibrium structure values to the zero-point vibrating molecule values, and further to the rotating–vibrating molecule at 300 K, for example. Eventually, these theoretical calculations will be made. In this work we address the problem of obtaining isolated-molecule absolute shielding for several ^{31}P-containing systems which are small enough for good ab initio calculations of magnetic properties. The success of the local-origin methods (GIAO [6], IGLO [7], LORG [8]) in calculations of ^{13}C, ^{15}N, ^{17}O, and ^{19}F shieldings have been properly gauged by comparison with an adequate set of experimental results [9]. Computations of nuclear shielding for ^{31}P require similar tests.

The primary ^{31}P standard is the PH_3 molecule for which molecular beam spectroscopy has provided $C_\perp = -114.90 \pm 0.13$ kHz, and $C_\parallel = -116.38 \pm 0.32$ kHz, where the quoted errors are 4σ or 99% confidence limits [10]. Davies et al. calculated from these a value $\sigma_e = 594.40$ ppm, by using the Flygare approximation for the diamagnetic shielding [11] of the ^{31}P in PH_3, which permits the relation

$$\sigma_e(PH_3) = \sigma^d(\text{free P atom}) + \sigma^{SR}(PH_3) \qquad (1)$$

to be written. The relation between σ^{SR} and C has been established by Ramsey [12] and by Flygare [13] to be

$$\sigma_{xx}^{SR} = \frac{C_{xx}}{G_{xx}} \frac{m_p}{2m_e g}, \qquad (2)$$

where G_{xx} is the molecular rotational constant, C_{xx} is the spin–rotation constant, and g is the nuclear g value which is 2.2632 for ^{31}P [14]. The yy and zz

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components are similarly related and σ^{SR} is the isotropic average of the three components.

In the past, the absolute ^{31}P shielding scale has been that reported by Appleman and Dailey [15], based on (a) the Davies et al. value of $\sigma_e(PH_3)$ from their spin–rotation constants, and (b) the measured chemical shift between the NMR reference substance for ^{31}P (85% $H_3PO_{4(aq)}$, cyl. $\perp B_0$) and liquid PH_3 at −90°C. The sum of (a) $\sigma_e = 594.4$ ppm for PH_3 and (b)

$$\frac{\sigma(85\%\ H_3PO_{4(aq)},\ \text{cyl.}\perp B_0) - \sigma(PH_3\,\text{liq}, -90^\circ C,\ \text{cyl.}\perp B_0)}{1-\sigma(85\%\ H_3PO_{4(aq)},\ \text{cyl.}\perp B_0)}$$

$$= -238\ \text{ppm}$$

was used to estimate

$$\sigma(85\%\ H_3PO_{4(aq)},\ \text{cyl.}\perp B_0) \approx 356\ \text{ppm}\,.$$

On this basis, chemical shifts relative to 85% $H_3PO_{4(aq)}$ have been converted to absolute shieldings. The Appleman and Dailey scale was adequate when shielding calculations were off by hundreds of ppm. It is now becoming possible to calculate ^{31}P shieldings with much better accuracy for molecules other than PH_3 [1]. Recent calculations of ^{31}P shielding in molecules have been reported for PH_3, [1,5,16–20], P_2H_4, P_2H_2, P_2, P_4, PH_2F, PHF_2, PF_3 [1], OPF_3, $O_2PF_2^-$, O_3PF^{2-}, HPO_4^{2-} [3], P_4, P_2, PN [21], PF_3, PF_4^+, PF_5, PF_6^-, PO_4^{3-} [4]. These calculations will undoubtedly improve with the use of ever larger basis sets in supercomputers. It becomes necessary to have a more accurate phosphorus shielding scale than the previous one which ignored the intermolecular effects on shielding.

We have previously studied the density dependence of ^{31}P shielding in pure PH_3 [22]. The previously reported shifts due to collisions of PH_3 with PH_3 are fairly large, 0.083 ppm per amagat (1 amagat is the density of an ideal gas at 1 atm and 273.16 K, i.e 2.687×10^{19} molecules cm^{-3}). From previous studies of chemical shifts as a function of density, it is our experience that in the range 0–50 amagat, the density dependence is linear, i.e.

$$\sigma(T,\rho) = \sigma_0(T) + \sum_i \sigma_1(T)_i\rho_i + \ldots\,. \tag{3}$$

The values of σ_1 for a nucleus in any one molecule depends on the collision partner, the light rare gases having the smallest effects on the shielding. To obtain chemical shifts which have less than 0.1 ppm intermolecular contributions, it would be sufficient to take spectra of individual samples at total densities of 1 amagat or less. At these densities, relaxation times for gas-phase ^{31}P NMR measurements are relatively short leading to broad lines in the spectra and a greater uncertainty in locating the center of the lines. To solve this problem, known amounts of an inert gas, argon, were added to all the samples to increase the relaxation time. Measurements could now be carried out with mixtures of the compounds at low densities (0.1–1.5 amagat) with only Ar present in large amounts (10–30 amagat). Within this range, one can safely assume a linear dependence of the chemical shift on the density of Ar; hence, with extrapolation, one can arrive at the chemical shift at the zero-density limit. Since σ_1 values involving Ar as collision partner are fairly small, the slopes will be less pronounced than would be the case in the pure gas of the ^{31}P-compounds, giving a more accurate extrapolation to zero density.

^{31}P spectra were obtained at 81.02 MHz in an IBM WP 200SY FT NMR spectrometer in sealed 4 mm (outer diameter) tubes containing mixtures of gases. The compounds were observed in groups of two or three per sample tube, the groupings depend on their chemical nonreactivity, with overlap between samples so that many molecules are observed in at least two different spectra. Four to five sample tubes were designated for each grouping, each sample tube differing only by the amount of Ar added.

PH_3 was used as a reference for the alkyl phosphines while PF_3 served as the standard for the halides after careful measurements of its shift relative to PH_3. The temperature was regulated to ±0.1 K at 300 K. Stability of the magnetic field was ascertained to ±0.005 ppm by monitoring the methyl protons in CH_3OH. Resolution of all spectra was at least 1 Hz/pt.

All the phosphorus compounds in this study were obtained commercially.

2. Results

The chemical shift obtained for PH_3 is significantly different from the reported shift in the liquid phase at 183 K, on which the old shielding scale was based [15]. This is not surprising because it is known from previous studies [22–24] that σ in ^{31}P is greatly affected by conditions which define the chemical environment of the molecules. For instance, it has been reported that there is a 4.2 ppm difference in the chemical shift of PH_3 upon increasing its density from the zero-pressure limit to 50 amagat at 300 K. In this study, a 1.1 ppm difference has been observed by going from zero density to 50 amagat in Ar at 300 K.

The resonance frequencies extrapolated to zero density in Ar are shown in fig. 1. The intercepts are used in the relation

$$\frac{\sigma_0(X)-\sigma_0(PF_3)}{1-\sigma_0(PF_3)}=\frac{\nu_0(PF_3)-\nu_0(X)}{\nu_0(PF_3)}\,. \qquad (4)$$

PF_3 is a suitable secondary standard since its chemical shift has a smaller dependence on the density of Ar than PH_3, its absolute frequency in the zero-density limit at 4.7 T can be obtained with better precision. The results of applying eq. (4) are shown in table 1. The liquid reference which is most commonly used for ^{31}P spectroscopy is 85% aqueous H_3PO_4. Although far from an ideal liquid reference, nearly all tabulations of condensed phase ^{31}P chemical shifts are based on this. The shielding difference between this liquid reference in a cylindrical sample with axis parallel to the magnetic field was determined relative to zero-density PF_3. Correction for bulk susceptibility of H_3PO_4 is −1.58 ppm, based on $\chi_V=-0.755\times10^{-6}$ cgs units [25].

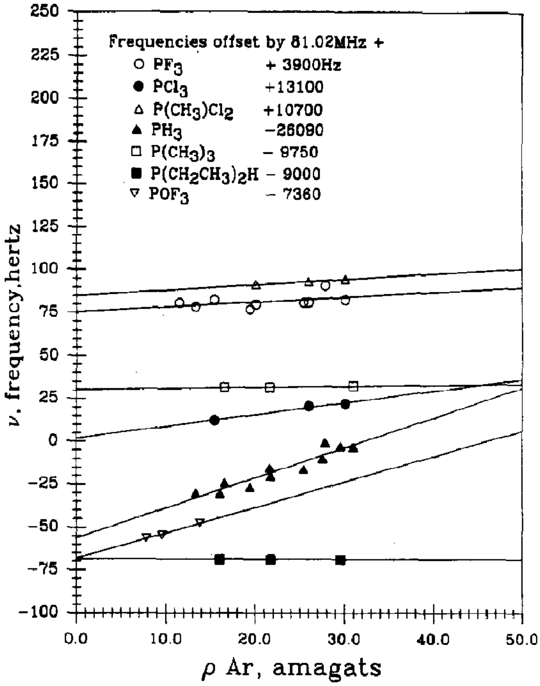

Fig. 1. Extrapolation of ^{31}P resonance frequencies in phosphorus compounds in argon gas to zero density of Ar. POF_3 samples were not diluted with argon, the plot was made against its own density.

Table 1
Thermal average ^{31}P shieldings in the zero-pressure limit

	$\sigma_0-\sigma_0(PF_3)$ (ppm) [a]
PH_3	371.76±0.14 [b]
PMe_3	169.02±0.01
PEt_2H	160.99±0.01
OPF_3	140.74±0.05
PF_3	0±0.05
PCl_2Me	−84.04±0.02
PCl_3	−111.40±0.07

[a] We also measured $\sigma(85\%\ H_3PO_{4(aq)},\ cyl.\|B_0)-\sigma_0(PF_3)=$ 108.82±0.05 ppm.

The absolute shielding of PH_3 arrived at in this work, based on the highly precise ^{31}P spin–rotation constants from molecular beam measurements for the PH_3 molecule in the ground vibrational states [10], using more accurate rotational constants [26,27] than previously available, and the ab initio diamagnetic parts (uncorrected for vibration) from Rothenberg et al. [28], does not differ from the earlier value by Davies et al. (594.45±0.63 ppm compared to their 594.40 ppm). The error quoted is based on Davies' conservative estimate of error in the spin–rotation constants at the 99% confidence level. The original ^{31}P shielding scale was based on the same absolute shielding for ^{31}P in the free PH_3 molecule. The flaw was in the use of the chemical shift measured in liquid PH_3 at −90°C.

The absolute shieldings obtained in this work are shown in table 2, where it is seen that 85% $H_3PO_{4(aq)}$ corrected to a spherical shape is 328.35 ppm rather than the old value of 356 ppm. The chemical shifts of these reported compounds in the zero-density limit are also shown in table 2, where the condensed phase data most frequently quoted in compilations of ^{31}P chemical shifts are compared against them. Differences of 9 and 28 ppm are found in PF_3 and PH_3, those molecules where the intermolecular effects in

Table 2
Thermal average absolute shielding values (ppm) in the free molecule at 300 K, based on $\sigma_0(PH_3, 300\ K) = 594.45 \pm 0.63$ ppm

	σ_0 (300 K) this work	δ [a] this work	δ [b] lit.	Ref.	σ other methods	Ref.	σ_e theor.	Ref.
PH_3	(594.45±0.63)	−266.10	−238±1 (liq, 183 K)	[37]			577.56–633.5	
			−245.4±0.1 (in THF)	[38]			(see table 3)	
PMe_3	391.71	−63.36	−62±1 (liq)	[37]			429.8	[50]
			−64.00 (liq crystal)	[39]				
PEt_2H	383.68	−55.33	−55.5 (liq)	[40]				
OPF_3	363.43	−35.08	−35 (liq)	[40]			384.6, 507	[50,3]
			−35.7±0.2 (liq crystal)	[41]				
PF_3	222.69	105.66	97 (liq, 203 K)	[42]			255, 372.5	[1,4]
PCl_2Me	138.65	189.70	193 (liq)	[40]				
PCl_3	111.29	217.06	220±1 (liq)	[37]	137 (liq, T_1)	[45]	150	[50]
PN					53 (molec. beam)	[46]	−74.8, −10	[50,29]
PH_4^+			−105.3 (in CH_3OH)	[44]	433.7 (from δ_{lit})		470.9, 483.3	[50,48]
PF_5			−80.3±0.1 (liq, 185 K)	[43]	408.6 (from δ_{lit})		442.6, 580.7	[50,4]
P_4			−551.5 (zero pressure, 526 K)	[24]	879.85 (from δ_{lit}) [c]		892, 885, 958.6	[1,29,29]
					817 (liq, T_1)	[47]		
P atom							961.14 nonrel.	[49]
85% $H_3PO_{4(aq)}$ (cyl. $\parallel B_0$)	331.51	−3.16						
85% $H_3PO_{4(aq)}$	328.35 [d]	0					353.9, 495.9 [e]	[50,4]

[a] $\sigma(300\ K) - \sigma(85\%\ H_3PO_{4(aq)}, sph)$. [b] σ (liq. or soln., T) $- \sigma(85\%\ H_3PO_{4(aq)}$, sph. or cyl. $\perp B_0)$. [c] 328.35 ppm added to δ_{lit}.

[d] Corrected for bulk susceptibility based on χ_V (85% $H_3PO_{4(aq)}$) $= -0.755 \times 10^{-6}$ cgs units [25], that is, $\sigma(85\%\ H_3PO_{4(aq)}, cyl. \parallel B_0) - \sigma(85\%\ H_3PO_{4(aq)}, sph) = 3.16$ ppm.

[e] PO_4^{3-} ion.

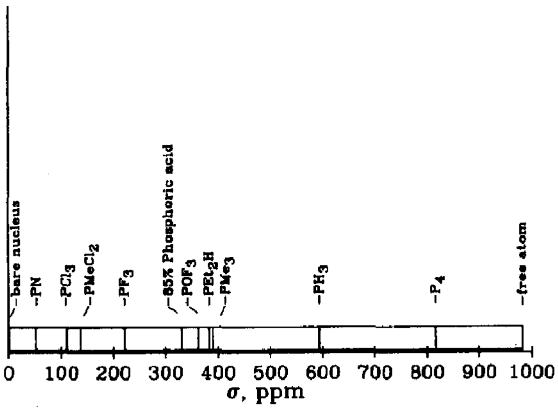

Fig. 2. ^{31}P absolute shielding scale.

argon gas are largest. The others differ by 3 ppm or less, well within the bulk susceptibility shifts in condensed phases. We did not attempt to repeat the experiment in P_4 at the zero-density limit. This chemical-shift value is known relative to $H_3PO_{4(aq)}$ corrected for bulk susceptibility [24]. The shielding scale is shown in fig. 2.

3. Discussion

Comparison with theory for $^{31}PH_3$ is given in table 3. It is quite clear that the large basis set calculations [1,3,16–18] without rovibrational averaging are in good agreement, on the average differing by only 8 ppm from experiment. It is also obvious that calculations in the other molecules, which have a larger number of electrons, show larger deviations from experiment. In table 2 the calculations with a common gauge origin [3,4,29] are as much as 150 ppm off whereas the IGLO method which uses local origins is 12–38 ppm off [1].

Only the isotropic absolute shielding can be determined from our measurements; the comparison of these with theory is not a fully adequate test of the theoretical calculations. In table 4 we combine our data with other experimental data to obtain the full tensor. When the molecule has an axially symmetric ^{31}P nuclear site, then from the anisotropy $\Delta\sigma$ and the isotropic average $\bar{\sigma}$ one can obtain $\sigma_\parallel$ and $\sigma_\perp$ to compare with calculations. The values of $\Delta\sigma$ (except in PN and PH_3) have been obtained in condensed phase and should not be combined with the $\bar{\sigma}$ obtained here at the zero-density limit without making corrections for intermolecular effects on $\Delta\sigma$. Nevertheless, we do this because the chemical shift accompanying the change of phase is of the same order of magnitude as the errors quoted for $\Delta\sigma$ in condensed phase. In table 4 we show the tensor components derived from our work and solid state or in liquid crystal $\Delta\sigma$ values. We make a comparison with theoretical values of $\sigma_\perp$ and $\sigma_\parallel$ at the equilibrium structure without making corrections for rovibrational averaging. Note that while the conventional CHF method [3] give $\Delta\sigma$ values only 60 ppm different from experiment, this is somewhat deceptive since individual components are 110–160 ppm off in OPF_3, and similarly for PF_3 [4]. On the other hand, although Fleischer et al. [1] give a value of $\Delta\sigma=316$ ppm which appears to have a worse agreement with their experimental $\Delta\sigma$, their individual components are much closer to experiment. From these examples, it appears that calculated $\sigma_\parallel$ are less accurate than $\sigma_\perp$ in PF_3. In summary, the best agreement of theory with experiment can be found in PH_3 and in P_4 molecules.

In table 5 we report the intermolecular effects due to collisions with Ar atoms. In our previous work we have noted that the intermolecular effects on ^{31}P chemical shifts in PH_3 molecule are largest. As we had expected, collisions with Ar atoms generally lead to smaller shifts than collisions with the ^{31}P-bearing molecules. The decrease in intermolecular effects in the order

$$PH_3\text{–}Ar > PCl_3\text{–}Ar \geqslant PF_3\text{–}Ar$$

may be attributed to a combination of factors. Firstly there are electrical terms in the intermolecular contributions to shielding [30] which increase with increasing dipole moment in the following order [31]:

$$PH_3 < PCl_3 < PF_3 .$$

Secondly there are van der Waals contributions to shielding which increase with increasing electric dipole polarizability in the following order:

$$PH_3 < PF_3 < PCl_3 .$$

Finally there is a site factor in intermolecular effects on shielding which increases upon increasing relative exposure of the ^{31}P nucleus in these molecules to the approaching Ar atom. Based on the known equilibrium geometry of PH_3 [32], PF_3 [33], and

Table 3
Comparison of theoretical calculations for ^{31}P shielding in PH_3 with experiment, all in ppm

Diamagnetic			Paramagnetic			$\sigma_\parallel$	$\sigma_\perp$	$\bar{\sigma}=\frac{1}{3}(\sigma_\parallel+2\sigma_\perp)$	$\sigma_\parallel-\sigma_\perp$	Ref.
$\sigma^d_\parallel$	$\sigma^d_\perp$	σ^d_{av}	$\sigma^p_\parallel$	$\sigma^p_\perp$	σ^p_{av}					
984.7	983.3	983.8	−421	−370	−387	564	612	597	−48	[11]
		980.28			−358.60			621.68		[19]
979.93	981.53	980.99	−364.15	−339.14	−347.48	615.78	642.39	633.51	−26.61	[20]
979.96	981.35	980.89	−416.21	−378.80	−391.27	563.75	602.55	589.62	−38.80	[18]
			−419.5	−384.4	−396.1	560.6	597.0	584.9	−36.4	[17]
980.36	981.85	981.35	−429.31	−388.34	−401.29	551.05	590.82	577.56	−39.77	[5] [b]
						576.2	609.0	598.1	−32.8	[16] [c]
						561.4	590.8	581	−29.4	[1] [c]
979.99	981.52	981.01	−422.86	−368.41	−386.56	557.13	613.11	594.45	−55.98	expt. [a]
			±1.10	±0.40	±0.63	±1.10	±0.40	±0.63	±1.5	
								594.40	−55±5	[10,51]

[a] Using spin-rotation constants from ref. [10] and rotational constants from refs. [26,27] and diamagnetic contributions from ref. [28]. Errors quoted are based entirely on quoted errors in the spin-rotation constants which are 4σ or 99% confidence. No error was assumed for the diamagnetic contribution, which is a non-relativistic, non-correlated calculation, as are all the other entries in the table.

[b] Gauge origin on P, for comparison with σ^p components from spin-rotation tensor calculations using gauge origin on center of mass, were also reported by these authors.

[c] Local origin methods do not permit separation into the same σ^p and σ^d contributions as the conventional CHF calculations with gauge origin on ^{31}P.

Table 4
Components of axially symmetric ^{31}P shielding tensors

Molecule	Experimental					Theoretical		
	this work $\bar{\sigma}$ zero-pressure limit	$\Delta\sigma$ liq. cryst. soln.	ref.	$\sigma_\perp=\bar{\sigma}-\frac{1}{3}\Delta\sigma$	$\sigma_\parallel=\bar{\sigma}+\frac{2}{3}\Delta\sigma$	$\sigma_\perp$ equil. geom.	$\sigma_\parallel$ equil. geom.	ref.
PMe_3	391.71	7.63±0.05	[39]	389.17	396.79			
OPF_3	363.43	284 ±15	[41]	268.77	552.75	291.2	571.5	[50]
						429.1	662.3	[38]
PF_3	222.72	181 ±15	[52]	162.39	343.38	150	466	[1]
						298.7	543.4	[4]
P_4	880 [a]	−405 ±15 [b]	[53]	1015	610	1042.3	591.3	[1]
						1114.4 [c]	647	[21]

[a] From $\sigma_0(300\ K)-\sigma(85\%\ H_3PO_{4(aq)}, sph)=551.5$ ppm [24]. [b] In solid white phosphorus.

[c] Gauge origin on P. $\sigma_\perp=1004$ ppm for gauge origin on center of mass.

PCl_3 [34], the bond gets longer and the molecule flattens out as the ligands become bulkier, all of which make the ^{31}P nucleus less exposed in collisions with Ar. The observed trend indicates that the site factor is the most important, and the polarizability is the next important factor.

Another recommended liquid reference is $P(OMe)_3$ under proton decoupling [35]. We find that its absolute shielding at 300 K for a cylindrical sample with axis parallel to the magnetic field is 189.95 ppm. When corrected for bulk susceptibility using $\chi_V=-0.575\times10^{-6}$ cgs units [36],

$$\sigma[P(OMe)_3, liq, 300\ K, sph.]=187.54\ ppm\ .$$

Incidentally, our standard sample of 85% aqueous H_3PO_4 appears at a frequency which converts to

Table 5
^{31}P chemical shifts due to collisions with argon atoms or with like molecules, ppb amagat^{-1} at 300 K, this work, corrected for bulk susceptibility

Molecule	With Ar	With self
PH_3	24.3 ±2.6	77.86±0.71 [a]
PMe_3	0.86±0.82	
PEt_2H	0.86±0.82	
OPF_3		24.4 ±2.0 [a]
PF_3	4.5 ±1.8	
PCl_2Me	4.87±0.82	
PCl_3	9.45±0.82	

[a] Previous reported values, with bulk susceptibility [36] correction are, PH_3: 81.0±2.5 ppb amagat^{-1} from ref. [22] and OPF_3: 9.6 ppb amagat^{-1} from ref. [23]. The former is in good agreement with present data, the latter appears to be in error.

$\Xi = 40480752$ Hz when corrected for bulk susceptibility.

4. Conclusions

We have measured ^{31}P shielding differences in the zero-pressure limit in selected compounds. We have established an absolute shielding scale for ^{31}P derived from gas-phase NMR measurements. The shielding information for these molecules may be used for evaluating theoretical values in the future. Comparison with presently available theoretical calculations show that calculations using local origins (such as the IGLO method) are in agreement with experiment to within about 20 ppm, whereas conventional calculations using a common gauge origin are typically 100–150 ppm away. Since the spin-rotation constants in PH_3 are precisely known, this absolute shielding scale is an accurate one, albeit based on a non-relativistic uncorrelated diamagnetic shielding calculation. The absolute shielding of 85% aqueous H_3PO_4 is 328.35 ppm and that of neat liquid $P(OMe)_3$ is 187.54 ppm, both at 300 K and both corrected for bulk susceptibility effects. These provide a way of converting measurements of chemical shift tensors to absolute shielding tensors.

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