

NUCLEAR MAGNETIC SHIELDING TENSORS FOR ^1H , ^{13}C , AND ^{15}N IN ORGANIC SOLIDS

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Abstract. A survey will be given of nuclear magnetic shielding tensors obtained by multiple pulse techniques for ^1H in carboxylic acids and by high field NMR for ^{13}C in carbonyl- and carboxyl groups of aromatic compounds and for ^{15}N in pyridine and nitrobenzene.

Solid state NMR for $I = 1/2$ nuclei has received considerable attention in the last years due to the development of new techniques by which an increase of resolution of solid state spectra can be achieved. This allows the determination of nuclear magnetic shielding tensors $\hat{\sigma}$ containing considerable more information than the isotropic shifts that can be measured in liquids. We have studied $\hat{\sigma}$ tensors for protons in a number of carboxylic acids by multiple pulse techniques at 90 MHz and for ^{13}C and ^{15}N in organic solids by high field NMR at 61 and 32 MHz, respectively. Some of the general features of the shielding tensors have become apparent regarding the size of the anisotropy as well as the orientation of the principal axes system of $\hat{\sigma}$ relative to the molecule.

For protons the largest values for the anisotropy of $\hat{\sigma}$ reported so far are found for protons in hydrogen bonds, the shielding tensors being almost axially symmetric. The values for the shielding anisotropy $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ are typically about 20 ppm in carboxylic acids. From single crystal studies (see, e.g. Haeberlen et al., 1974) it follows that the unique axis of the $\hat{\sigma}$ tensor which is also the most shielded direction, lies along the hydrogen bond. We have shown that these features of the $\hat{\sigma}$ tensor for protons in hydrogen bonds are due mainly to the diamagnetic effect (Haeberlen et al., 1974), which can be handled quantitatively as described by Gierke and Flygare, 1972.

^{13}C shielding tensors were studied for carbons involved in carbonyl and carboxyl groups (Kempf et al., 1974) as shown in Table 1. The most shielded direction is perpendicular to the sp^2

Compound	σ_{xx} (ppm)	σ_{yy} (ppm)	σ_{zz} (ppm)
Benzophenone	-79	-36	+94
Benzoic Acid	-38	+ 5	+90
Silver Benzoate	-53	+18	+101
Benzoic Acid Anhydride	-42	+50	+114

Table 1: Principal elements of ^{13}C shielding tensors relative to CS_2 , estimated accuracy ± 4 ppm.

plane. From these data and the values for the corresponding aliphatic compounds (Waugh et al., 1972) it follows that both the components of largest and smallest shielding, σ_{zz} and σ_{xx} respectively, vary relatively little in this series, whereas the value for the intermediate shielding can be anywhere between -71 and +78 ppm (see also Table 1). For ^{13}C the main features of the shielding anisotropy are governed by the paramagnetic contribution. The

much larger variation of σ_{yy} compared with σ_{xx} and σ_{zz} in this series can be understood if one assumes that the y-axis generally is close to the C = O bond as observed in single crystals of benzophenone and benzoic acid (Kempf et al., 1972, 1974). This was further supported by studying the ^{13}C

shielding anisotropy in thiobenzophenone so that the shielding components for a C = O and for a C = S group could be correlated with the corresponding optical spectra (Kempf et al., 1974).

The determination of ^{15}N shielding anisotropies allows a comparison of the values for $\Delta\sigma$ for ^{13}C and ^{15}N in isoelectronic compounds (Table 2).

Isoelectronic Pair	$\Delta\sigma$ [ppm]		References
	^{13}C	^{15}N	
benzene/pyridine	180 ^a	672	^a Pines, A., Gibby, M.G., Waugh, J.S., 1972, Chem.Phys.Letters, <u>15</u> , 373.
Ag Benzoate/nitrobenzene	-112	-398	^b Lauterbur, P.C., 1958, Phys.Rev.Letters, <u>1</u> , 343.
$\text{CO}_3^{2-}/\text{NO}_3^-$	75 ^b	210 ^c	^c Gibby, M.G., Griffin, R.G., Pines, A., Waugh, J.S., 1972, Chem.Phys.Letters, <u>17</u> , 80
CO/ N_2	401 ^d	635 ^e	^d Ozier, I., Crapo, K.M., Ramsey, N.F., 1968, J.Chem.Phys., <u>49</u> , 2314.
			^e Baker, M.R., Anderson, C.H., Ramsey, N.F., 1964, Phys.Rev. <u>133 A</u> , 1533.

Table 2: Anisotropy of the shielding for ^{13}C and ^{15}N in isoelectronic systems. For details see Schweitzer and Spiess, 1974.

Despite of the limited material available now, it seems to be clear that the shielding anisotropy in general is substantially larger for ^{15}N (Schweitzer and Spiess, 1974). The large increase in $\Delta\sigma$ for ^{15}N compared with ^{13}C for the first three pairs (Table 2) seems to be especially interesting. For the pyridine/benzene pair one might be tempted to attribute this increase to the existence of the non-bonding orbital at the nitrogen atom in pyridine in contrast to benzene. The data for nitrobenzene and the nitrate ion show, however, that the increase in $\Delta\sigma$ is almost as big in these cases where no such simple explanation is obvious.

These results show that by studying shielding tensors for different nuclei and for series of compounds some general features can be established so that from the experimental determination of shielding components one will get meaningful information about the electronic structure of molecules.

References.

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