

PROTON-ENHANCED NUCLEAR INDUCTION SPECTROSCOPY. ¹³C CHEMICAL SHIELDING ANISOTROPY IN SOME ORGANIC SOLIDS*

A. PINES**, M.G. GIBBY*** and J.S. WAUGH

*Department of Chemistry and Research Laboratory of Electronics, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, USA*

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Using the recently introduced technique of proton-enhanced nuclear induction spectroscopy, ¹³C chemical shielding parameters are reported for a number of simple organic compounds, and some exemplary spectra are shown. The ¹³C chemical shielding parameters are sensitive to the functional character of the carbon and to molecular structure. Several interesting aspects of these experiments, including molecular motion and cross-relaxation effects, are mentioned briefly.

It is well known that NMR spectra from solids offer a wealth of molecular information which is partially averaged in liquids and liquid crystals due to rapid molecular reorientation. An important example is the chemical shielding tensor, for which liquid spectra provide only a measurement of the trace. A measurement of the full tensor would be extremely valuable but is normally difficult in solids due to strong dipolar broadening. We recently demonstrated a technique in which the problem of resolution is overcome by observing dilute spins (*S*) decoupled from abundant spins (*I*), and the consequent loss in sensitivity is compensated for by cross polarization from the *I* to the *S* spins [1] †. Using this approach, we have obtained high resolution NMR spectra of natural abundance ¹³C from an extensive series of organic compounds in the solid state, and we present here a preliminary report of some typical results. A full report will be presented elsewhere [3].

Table 1 summarizes shielding parameters for ¹³C

in some simple organic compounds. Evidently, the elements of the shielding tensor σ are a much more sensitive probe into molecular structure than the trace alone. For example, methyl group isotropic shifts are dominated by shifts of σ_{11} and σ_{22} , while σ_{33} remains practically constant from one compound to the next; this could hardly be invoked from liquid measurements. Note also the sensitivity of σ_{22} for the carbonyl carbon to substituents. Another noticeable effect is the downfield isotropic shift in going from liquid to solid phase. This is particularly dramatic for hexafluorobenzene. Fig. 1 shows an exemplary spectrum from which the data of table 1 were extracted. These were obtained usually in less than 10 minutes from natural abundance ¹³C in samples containing ≈ 250 mg of material.

These results indicate clearly that it is more profitable to obtain NMR spectra from low temperature solid samples by our method than by normal Fourier transform spectroscopy from liquids. In addition to the more complete information, the signal-to-noise ratios are considerably greater due to the combination of low temperature and cross-polarization procedure. A quantitative analysis of this point will be presented separately. Isotropic sharp-line spectra may still be obtained in more complicated molecules by combining this technique with sample-spinning at the magic angle [4].

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** Address after August 31, 1972: Department of Chemistry, University of California, Berkeley, California 94720, USA.

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† The double resonance procedure is due to Hartmann and Hahn [2].

Table 1
Typical ^{13}C chemical shielding parameters in organic compounds^{a)}

Compound	Formula ^{b)}	T (°C)	Carbon 1 ^{c)}				
			σ_{11}	σ_{22}	σ_{33}	$\bar{\sigma}$	σ_i
ethanol	$\text{C}^1\text{H}_3\text{C}^2\text{H}_2\text{OH}$	-170	104 ± 6	113 ± 6	128 ± 6	115 ± 6	110
dimethyl sulphoxide	$(\text{C}^1\text{H}_3)_2\text{SO}$	-47	63 ± 7	85 ± 6	111 ± 7	86 ± 7	86
dimethyl disulphide	$(\text{C}^1\text{H}_3\text{S})_2$	-186	81 ± 6	111 ± 6	123 ± 6	105 ± 6	109
diethyl ether	$(\text{C}^1\text{H}_3\text{C}^2\text{H}_2)_2\text{O}$	-140	100 ± 6	110 ± 6	124 ± 6	111 ± 6	113
acetaldehyde	$\text{C}^1\text{H}_3\text{C}^3\text{HO}$	-186	74 ± 6	86 ± 6	126 ± 7	95 ± 6	96
acetone	$(\text{C}^1\text{H}_3)_2\text{C}^3\text{O}$	-186	81 ± 6	81 ± 6	131 ± 6	98 ± 6	98
acetic acid	$\text{C}^1\text{H}_3\text{C}^3\text{OOH}$	-186	83 ± 6	83 ± 6	118 ± 6	95 ± 6	108
acetic anhydride	$(\text{C}^1\text{H}_3\text{C}^3\text{O})_2\text{O}$	-182	90 ± 6	93 ± 6	128 ± 6	103 ± 6	106 ± 6
methyl acetate	$\text{C}^1\text{H}_3\text{C}^3\text{OOC}^2\text{H}_3$	-140	86 ± 6	89 ± 6	107 ± 6	95 ± 6	107
dimethyl acetylene	$(\text{C}^1\text{H}_3\text{C}^3)_2$	-186	113 ± 6	113 ± 6	127 ± 6	118 ± 6	124 ± 6
toluene	$\text{C}_6^3\text{H}_5\text{C}^1\text{H}_3$	-186	96 ± 6	107 ± 6	124 ± 6	109 ± 6	107
hexamethylbenzene	$(\text{C}^3\text{C}^1\text{H}_3)_6$	-186	104 ± 16	104 ± 16	104 ± 16	104 ± 16	104 ± 16
		23	107 ± 14	107 ± 14	107 ± 14	107 ± 14	
hexamethyl dewar benzene	$(\text{C}^3\text{C}^1\text{H}_3)_4(\text{C}^2\text{C}^1\text{H}_3)_2$	-186	118 ± 8	118 ± 8	118 ± 8	118 ± 8	118 ± 6

		Carbon 2					
		σ_{11}	σ_{22}	σ_{33}	$\bar{\sigma}$	σ_i	
methanol	$\text{C}^2\text{H}_3\text{OH}$	-186	55 ± 6	55 ± 6	118 ± 6	76 ± 6	80
ethanol	$\text{C}^1\text{H}_3\text{C}^2\text{H}_2\text{OH}$	-170	56 ± 6	56 ± 6	113 ± 16	75 ± 9	71 ± 6
diethyl ether	$(\text{C}^1\text{H}_3\text{C}^2\text{H}_2)_2\text{O}$	-140	31 ± 6	43 ± 6	110 ± 15	61 ± 9	63 ± 6
methyl formate	$\text{HC}^3\text{OOC}^2\text{H}_3$	-186	53 ± 6	65 ± 7	121 ± 6	80 ± 6	79
methyl acetate	$\text{C}^1\text{H}_3\text{C}^3\text{OOC}^2\text{H}_3$	-140	37 ± 6	53 ± 6	121 ± 6	70 ± 6	77
dimethyl carbonate	$\text{C}^3\text{O}(\text{OC}^2\text{H}_3)_2$	-186	50 ± 6	56 ± 6	121 ± 6	76 ± 6	79
hexamethyl dewar benzene	$(\text{C}^3\text{C}^1\text{H}_3)_4(\text{C}^2\text{C}^1\text{H}_3)_2$	-186	57 ± 6	72 ± 6	86 ± 6	72 ± 6	72 ± 6

		Carbon 3					
		σ_{11}	σ_{22}	σ_{33}	$\bar{\sigma}$	σ_i	
acetaldehyde	$\text{C}^1\text{H}_3\text{C}^3\text{HO}$	-186	-147 ± 7	-105 ± 6	42 ± 6	-70 ± 6	-72
acetone	$(\text{C}^1\text{H}_3)_2\text{C}^3\text{O}$	-186	-150 ± 6	-136 ± 6	50 ± 7	-79 ± 6	-78
acetic acid	$\text{C}^1\text{H}_3\text{C}^3\text{OOH}$	-186	-140 ± 6	-55 ± 6	19 ± 6	-59 ± 6	-49
acetic anhydride	$(\text{C}^1\text{H}_3\text{C}^3\text{O})_2\text{O}$	-182	-152 ± 6	13 ± 6	13 ± 6	-42 ± 6	-38
methyl formate	$\text{HC}^3\text{OOC}^2\text{H}_3$	-186	-124 ± 6	-7 ± 7	22 ± 7	-36 ± 7	-32
methyl acetate	$\text{C}^1\text{H}_3\text{C}^3\text{OOC}^2\text{H}_3$	-140	-138 ± 6	-31 ± 6	9 ± 6	-53 ± 6	-43
dimethyl carbonate	$\text{C}^3\text{O}(\text{OC}^2\text{H}_3)_2$	-186	-102 ± 9	19 ± 6	19 ± 6	-21 ± 7	-29
dimethyl acetylene	$(\text{C}^1\text{H}_3\text{C}^3)_2$	-186	-29 ± 6	-29 ± 6	173 ± 17	38 ± 8	51 ± 6
benzene	C_6^3H_6	-50	-63 ± 1	-63 ± 1	117 ± 1	-3 ± 1	0
toluene	$\text{C}_6^3\text{H}_5\text{C}^1\text{H}_3$	-186	-93 ± 7	-6 ± 6	132 ± 6	11 ± 6	3 ± 6
hexamethylbenzene	$(\text{C}^3\text{C}^1\text{H}_3)_6$	-186	-104 ± 6	-26 ± 6	104 ± 16	-9 ± 9	
		23	-61 ± 6	-61 ± 6	107 ± 14	-5 ± 9	
hexamethyl dewar benzene	$(\text{C}^3\text{C}^1\text{H}_3)_4(\text{C}^2\text{C}^1\text{H}_3)_2$	-186	-115 ± 6	-20 ± 6	74 ± 22	-20 ± 12	-17 ± 6
hexafluorobenzene	C_6^3F_6	-40	-42 ± 6	-42 ± 6	-2 ± 8	-29 ± 7	-7 ± 7
		-170 ^{d)}	-37 ± 8	-37 ± 8	2 ± 10	-24 ± 9	-7 ± 7
carbon disulphide ^{e)}	C^3S_2	-200	-205 ± 10	-205 ± 10	220 ± 14	-63 ± 11	-65

a) The errors in the anisotropies are considerably smaller than those for the absolute values of the shielding parameters.

b) C^α indicates carbon number α .

c) Shifts are in ppm relative to benzene liquid. $\bar{\sigma} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ and σ_i is the isotropic shift in the neat liquid at room temperature.

d) At this temperature, one third of the molecules are alleged to be rigid on our time scale [9]. There is indeed a noticeable broadening of our line, but any axial asymmetry in the chemical shielding tensor is too small to resolve. This will be discussed later in more detail.

e) From ref. [10].

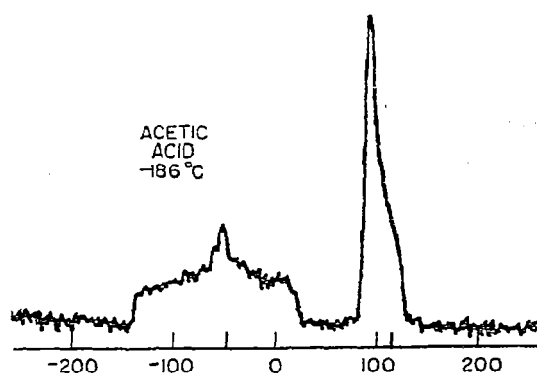


Fig. 1. Proton-enhanced nuclear induction spectra of natural abundance ^{13}C in solid acetic acid. The horizontal scale is in ppm from an external reference of liquid benzene. The two thicker marks on this axis indicate the positions of the two ^{13}C lines in neat acetic acid at room temperature. Spectra with similar signal/noise were obtained from all compounds studied, typically in less than 10 minutes from ≈ 250 mg material. ^{13}C resonance frequency is 24.46 MHz.

We have studied other aspects of this experiment which should prove very useful in studies of molecular solids. These include:

(i) Assignment of σ_{ii} to directions in the molecular frame. This is done in several ways including single crystal studies and by utilizing dipolar splitting from a third unlike nucleus (e.g., ^2H , ^{14}N , etc.). The latter is useful since it does not require crystals and depends only on the known orientation of the principal axes of the dipolar interaction tensor. In some cases, symmetry is an aid — note for example, that in *most* methyl groups the most shielded component, σ_{33} , is along the C_{3v} symmetry axis.

(ii) Cross relaxation. Since the dynamics of polarization transfer from I to S spins depends strongly on the site geometry of the S spin, such a study is extremely valuable for spectral assignments in much the same way that T_1 experiments are used in liquid studies [5]. This should also be useful in powder spectra for determination of the principal axes of the shielding tensor as in (i) above. We have indeed observed quantitative cross-relaxation effects in a number of cases.

(iii) Molecular motion. High resolution spectral changes are quite versatile in studying molecular motion in the solid as are second moment and spin-lattice relaxation studies of the wideline spectra.

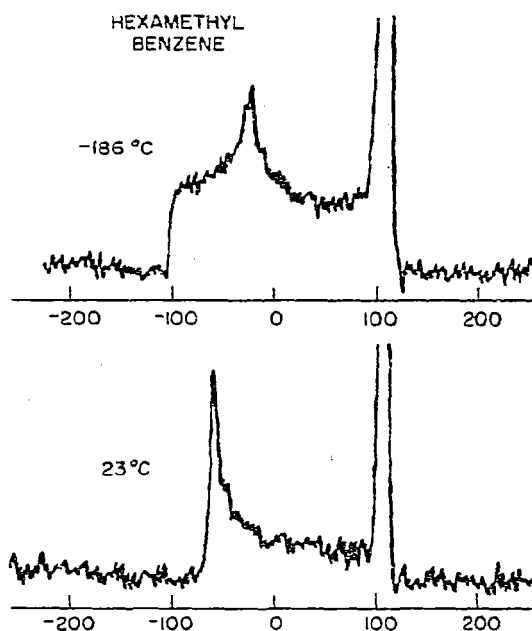


Fig. 2. Proton-enhanced nuclear induction spectra of natural abundance ^{13}C in hexamethylbenzene in the rigid phase (-186°C) and in the rotor phase (23°C). The high field peak is from the methyl groups and is not shown in detail. The asymmetric pattern for the low field ring carbons at -186°C collapses into an axially symmetric one at 23°C due to rapid reorientation about the C_6 axis. This indicates that the most shielded component σ_{33} is perpendicular to the plane of the ring. Other details are as in fig. 1.

Fig. 2 shows the effect of molecular motion in hexamethylbenzene on the ^{13}C spectrum. The high temperature spectrum corresponds to rapid motion about the six-fold axis leading to an averaging of the two low-field elements; thus σ_{33} for the ring carbons (the most shielded component) corresponds to an axis perpendicular to the molecular plane. Temperature-dependent studies of this transition yield detailed information on the kinetics of the reorientation process. The anisotropy $\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22})$ is 170 ppm for the ring carbons which is close to the value of 180 ppm for benzene in the rotor phase (see table 1 and ref. [6]).

We believe that these and forthcoming results can provide a reliable check for data obtained by other techniques such as liquid crystal studies [7], and field- and temperature-dependent studies of ^{13}C nuclear spin relaxation [8]. It is hoped that they will stimulate

an effort on the part of theoreticians to provide calculations of these parameters.

The experiments were performed with a crossed coil probe producing rotating rf fields of ≈ 10 G for ^1H and 40–50 G for ^{13}C . The ^{13}C operating frequency was 24.46 MHz. Mixing time for the cross-polarization step varied from 3 to 20 msec. Details of the apparatus and procedures used will be provided in the near future.

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