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Model Calculations of the ^{13}C NMR Shieldings in the Crystalline Cyclic Pentamer of Poly(*p*-phenylene sulfide)

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ABSTRACT: The cyclic pentamer of poly(*p*-phenylene sulfide) [c-(PS)$_5$] cystallizes in an interesting manner. Though only a single c-(PS)$_5$ molecule constitutes the asymmetric unit of its crystalline unit cell, the conformation about and the geometry of the C−S bonds vary widely around the cycle. The high-resolution, solid-state ^{13}C NMR spectrum of c-(PS)$_5$ reflects this heterogeneity of structural environments, where multiple resonances (at least six) are observed for both protonated (C$_P$) and nonprotonated (C$_Q$) carbons spread over 18 and 8 ppm chemical shift ranges, respectively. Crystalline c-(PS)$_5$ provides us with a unique model system with which we may test our ability to calculate NMR nuclear shieldings with ab initio quantum mechanical methods. For this purpose, a gauge including atomic orbital (GIAO) approach was implemented with the use of locally dense basis sets. Diphenyl sulfide was adopted as a fragment model for c-(PS)$_5$, with the S, C$_Q$, and two C$_P$ atoms on a single adjacent phenyl ring treated with the locally dense 6-311G(d,p) basis set, while the remaining atoms were treated at the 3-21G level. This approach required 10 calculations to treat each of the structurally unique S−C$_Q$−(C$_P$)$_2$ fragments in c-(PS)$_5$. Calculated nuclear shieldings and a ^{13}C NMR spectrum generated from them resemble the observed ^{13}C NMR spectrum of crystalline c-(PS)$_5$. The calculated nuclear shieldings are strongly correlated with the conformation (dihedral angle) about the C$_Q$−S bonds, exhibiting a $\cos^2 \theta_{PQ}$ dependence on the dihedral angle θ_{PQ}. Application of the same conformational dependence of nuclear shieldings found for c-(PS)$_5$ to crystalline and liquid diphenyl sulfide permitted an understanding of their observed ^{13}C NMR spectra as well as their rigid, crystalline and flexible, liquid state conformations.

Introduction

The resonance frequencies of carbon nuclei observed in high-resolution ^{13}C NMR spectra of solid polymers have been successfully interpreted in terms of their local, rigid conformational environments.[1] As an example, poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) crystallizes[2,3] in the all-trans, planar zigzag conformation, where all oxygen atoms lie in the same plane, while the phenyl rings are successively inclined at ±45° with respect to this plane (see Figure 1). As a consequence, one of the protonated aromatic carbons C$_P$ is close, at a dihedral angle of 45°, to the nonprotonated carbon C$_Q$ of the adjacent phenyl ring, while the other C$_P$ lies at a dihedral angle of 135° and is farther removed from the same C$_Q$ (see Figure 2).

It is not surprising that the asymmetric environments experienced by the C$_P$ carbon nuclei in crystalline PDMPO result[4] in resonant ^{13}C frequencies which differ by some 5 ppm. However, poly(*p*-phenylene sulfide) (PPS), which crystallizes[5,6] in the same conformation as PDMPO, manifests[7] only a single resonance for its C$_P$ carbon nuclei. In an effort to understand the difference in the sensitivity of C$_P$ carbon resonance frequencies in these two polymers with the same crystalline conformation, we observed[7] the high-resolution ^{13}C NMR spectrum of the crystalline cyclic pentamer of PPS, c-(PS)$_5$, whose crystalline conformation is known[8] from single-crystal X-ray diffraction analysis (see Figure 3). It is clear from the drawing that the local conformational environment about each sulfur atom is distinct; i.e., the mutual orientations of phenyl rings attached to common sulfur atoms vary for all five S atoms in crystalline c-(PS)$_5$. The dihedral angles between C$_P$ and C$_Q$ carbons across the pair of intervening C$_Q$−S and S−C$_Q$ bonds at each sulfur are summarized in Table 1, and make apparent the heterogeneity in the local conformational environments about each of the five sulfur atoms in c-(PS)$_5$.

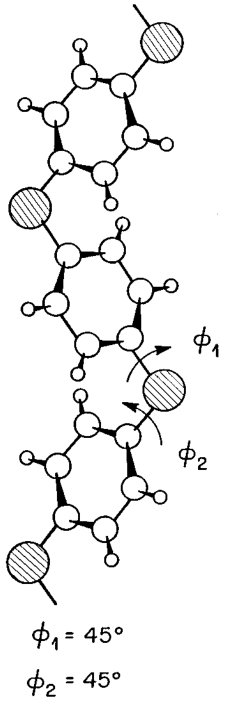

Figure 1. Schematic drawing of the crystalline conformation of PPS,[5,6] which is the same for crystalline PDMPO.[2,3]

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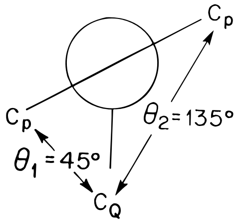


Figure 2. Newman projection along the C_Q−S bond of the crystalline conformation of PPS.

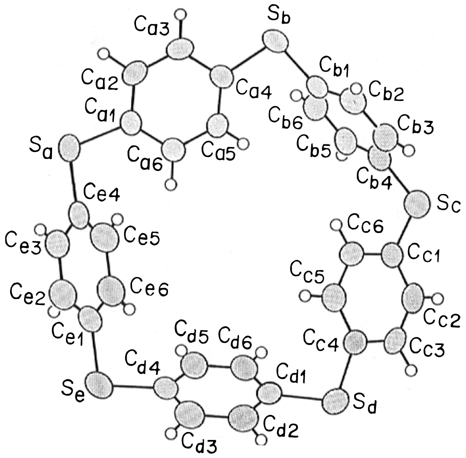


Figure 3. Crystalline conformation of c-(PS)$_5$.[8]

Table 1. Dihedral Angles (θ_{PQ}) between the P and Q Ring Carbons in Crystalline c-(PS)$_5$

C_P[a]	C_Q[a]	θ_{PQ} (deg)	C_P[a]	C_Q[a]	θ_{PQ} (deg)
c$_6$	b$_4$	1	b$_5$	c$_1$	101
a$_5$	b$_1$	4	b$_2$	a$_4$	102
a$_6$	e$_4$	24	d$_3$	e$_1$	116
c$_5$	d$_1$	36	e$_3$	a$_1$	129
d$_6$	c$_4$	41	e$_2$	d$_4$	131
e$_6$	d$_4$	51	d$_2$	e$_4$	142
e$_5$	a$_1$	54	c$_3$	d$_1$	148
d$_5$	e$_1$	66	a$_2$	e$_4$	160
b$_3$	c$_1$	77	a$_3$	b$_1$	178
b$_6$	a$_4$	78	c$_2$	b$_4$	179

[a] See Figure 3 for the labeling of atoms in c-(PS)$_5$.

The high-resolution, solid-state ^{13}C NMR spectrum of crystalline c-(PS)$_5$ exhibits[7] multiple resonances, at least six for both the C_P and C_Q carbons, which are spread over 8 ppm for the C_Q and 18 ppm for the C_P carbons. Note that the dihedral angles between the C_P and C_Q carbons (θ_{PQ}) nearly span the full range from $\theta_{PQ} = 0°$ to 180°, i.e., from the cis (0°) to the trans (180°) arrangement. If the multiple resonances observed for the C_P and C_Q carbons in c-(PS)$_5$ originated exclusively from the different arrangements of phenyl rings about the C−S bonds in the crystalline conformation (see Figure 3), then the difference in shielding between a cis ($\theta_{PQ} = 0°$) and a trans ($\theta_{PQ} = 180°$) arrangement of C_P and C_Q would be expected to be 8 and 18 ppm for the Q and P carbons, respectively, based on the following observations.

It is observed in crystalline di- and trimethoxybenzenes[9−12] that a cis arrangement of methyl and protonated ring carbons produces a 6 ppm shielding of C_P relative to their trans arrangement, consistent with the 5 ppm difference in C_P chemical shifts observed[4] in PDMPO, where $\theta_{PQ} = 45°, 135°$. When these observations are coupled with the absence of C_P carbon resonance splitting (<1.5 ppm) observed[7] in PPS, where θ_{PQ} is also 45°, 135°, they strongly suggested that the 18 ppm spread in C_P chemical shifts observed for c-(PS)$_5$ is not exclusively a consequence of its crystalline conformation.

Table 2. C_P−C_Q−S Valence Angles in Crystalline c-(PS)$_5$.

(P	Q	S)[a]	<C_P−C_Q−S_X	(P	Q	S)[a]	<C_P−C_Q−S_X
a$_2$	a$_1$	a	116.1	c$_3$	c$_4$	d	118.7
a$_6$	a$_1$	a	124.4	c$_5$	c$_4$	d	123.0
a$_3$	a$_4$	b	115.6	d$_2$	d$_1$	d	118.1
a$_5$	a$_4$	b	125.6	d$_6$	d$_1$	d	122.3
b$_2$	b$_1$	b	118.9	d$_3$	d$_4$	e	121.1
b$_6$	b$_1$	b	121.4	d$_5$	d$_4$	e	119.5
b$_3$	b$_4$	c	119.5	e$_2$	e$_1$	e	120.2
b$_5$	b$_4$	c	120.9	e$_6$	e$_1$	e	120.8
c$_2$	c$_1$	c	116.9	e$_3$	e$_4$	a	117.6
c$_6$	c$_1$	c	124.3	e$_5$	e$_4$	a	122.9

[a] See Figure 3 for atom numbering.

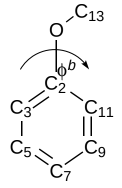
Another likely source of the dispersion in C_P resonances is the variety of C_P−C_Q−S valence angles observed[8] in crystalline c-(PS)$_5$. Table 2 shows that the pair of C_P−C_Q−S valence angles adjacent to the same C_Q range from nearly symmetric (120.2°, 120.8°) to highly asymmetric (115.6°, 125.6°). In addition, the C_Q−S−C_Q valence angles vary from 100.1° to 104.0° and may contribute to the dispersion of resonance frequencies observed for the C_P carbons.

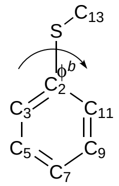
Crystalline c-(PS)$_5$ provides us with a unique experimental model system with which we may test our ability to calculate NMR chemical shieldings via ab initio quantum mechanical methods.[13,14] Single-crystal X-ray diffraction provides us with a detailed description of the heterogeneous conformational and structural environments occurring in the crystals of c-(PS)$_5$,[8] and high-resolution, solid-state ^{13}C NMR makes apparent that these heterogeneous environments are manifested as large dispersions in the resonance frequencies of both C_P (18 ppm) and C_Q (8 ppm) carbon nuclei. Because a single c-(PS)$_5$ molecule constitutes the asymmetric unit of its crystalline unit cell, all comparisons between observed and calculated ^{13}C NMR shieldings can be made on a single c-(PS)$_5$ molecule, thereby avoiding the usual comparison of observed and calculated resonance frequencies for a homologous series of different compounds.

Preliminary ab initio quantum mechanical NMR shielding calculations carried out with the GIAO program based on Ditchfield's gauge including atomic orbital method[15] were conducted for the model compounds methoxybenzene (MB) and methyl phenyl sulfide (MPS), with very encouraging results (see Table 3). In the coplanar conformation of MB, the calculated difference in shielding of the ortho C_P carbons, which are either cis or trans to the methyl carbon, was 4.4 ppm compared to the observed[9−12] value of 6 ppm. On the other hand, for MPS, the same splitting calculated for the planar conformer was 1.3 ppm. This is consistent with the absence of C_P carbon resonance splitting (<1.5 ppm) observed[7] in the PPS polymer, while an ca. 5 ppm splitting is observed[4] in the PDMPO polymer.

In addition, the relative shieldings calculated for all the phenyl ring carbons (Q, O, M, P) in MB and MPS are in close agreement for each compound and between compounds with those observed[16,17] by liquid state ^{13}C NMR. It appears that the accuracy, in particular the relative accuracy, of the quantum mechanical ^{13}C chemical shifts calculated for the PPS and PDMPO model compounds is more than sufficient to warrant similar calculations for the ^{13}C chemical shifts of crystalline c-(PS)$_5$.

Table 3. Comparison of Calculated and Observed ^{13}C Chemical Shifts for PDMPO Model Compounds[a]





	$\phi = 0°$	$\phi = 90°$	ave	obs	$\phi = 0°$	$\phi = 90°$	ave	obs
C_2	32.5	32.0	32.3	25.2	48.9	54.4	51.7	45.5
C_3	76.5	68.3	73.5	70.9	66.4	51.8	59.4	57.4
C_{11}	80.9	68.3			67.7	51.8		
C_5	57.1	58.3	57.8	55.4	59.8	61.2	60.5	55.4
C_9	57.6	58.3			59.7	61.2		
C_7	70.6	66.4	68.5	64.3	65.5	59.0	62.3	59.2
C_{13}	146.1	138.9	142.5		179.2	172.9	176.1	
calculated vs observed								
mean error				4.1				4.1
standard deviation				2.2				1.9
rmse				4.5				4.4

[a] Observed[16,17] shifts have been converted to absolute shifts by comparison to the absolute shift of liquid TMS of 184.1 ppm.[18] [b] $\phi = 0$ when C_{11} and C_{13} are cis.

The unique crystalline structure of c-(PS)$_5$ should provide a stringent test of our ability to calculate ^{13}C NMR chemical shifts. We shall learn what chemical shift effects are produced by geometrical ($\angle C_P-C_Q-S$, $\angle C_Q-S-C_Q$) and conformational (θ_{PQ}) variations and enhance our ability to interpret solid-state ^{13}C NMR spectra of solids that cannot be obtained as single crystals, which include virtually all synthetic polymer samples.

Calculation of Nuclear Shieldings

It is simply impossible at the present time to calculate the chemical shieldings of nuclei in a molecule as large as c-(PS)$_5$ even using the locally dense basis set approach.[19,20] What we were able to do was carry out a series of calculations on diphenyl sulfide. We employed the locally dense basis set approach,[19,20] where the large 6-311G(d,p) basis was used for the S atom and the C_Q and the two C_P carbons of one of the adjacent phenyl rings and the 3-21G basis for all other atoms. Ten calculations were carried out matching the ten experimentally observed[8] configurations (conformations and molecular geometries) occurring on either side of each sulfur atom in crystalline c-(PS)$_5$.

Results and Discussion

In Figure 4 a comparison of observed (Exp) and calculated ($C_P + C_Q$) ^{13}C NMR spectra is presented, where the calculated spectra were obtained from the ab initio quantum mechanical nuclear shieldings by assuming Lorentzian line shapes whose widths at half-height are 1 ppm. Note that the total spread and distribution of resonance peaks in the observed and calculated spectra of c-(PS)$_5$ are reasonably similar. On the other hand, it must be mentioned that the observed spectrum has been uniformly shifted 10 ppm upfield to achieve the comparison shown in Figure 4, implying that the calculated nuclear shieldings seem to be overestimated by ca. 8% (see ref 21) compared to those observed in the crystals of c-(PS)$_5$.

No correlations between the calculated nuclear shieldings and variations in molecular geometries ($\angle C_P-C_Q-S$ or $\angle C_Q-S-C_Q$) occurring around the 5 S atoms in c-(PS)$_5$ were detected. Instead, the calculated nuclear shieldings appear to be strongly correlated with the conformation (dihedral angle) about the C−S bonds. Figures 5 and 6 show plots of relative ^{13}C chemical shifts calculated for the C_P and C_Q carbons as a function of the dihedral angle θ_{PQ} about the C−S bond. For both carbon types, the calculated nuclear shieldings (or δ ^{13}Cs) follow a cos $^2\theta_{PQ}$ dependence. At present we have no underlying molecular explanation for this behavior, but this does not mean that we cannot utilize the conformational sensitivity of nuclear shieldings uncovered by our calculations to interpret the ^{13}C NMR spectra of molecules containing similar constituent fragments in terms of their conformations.

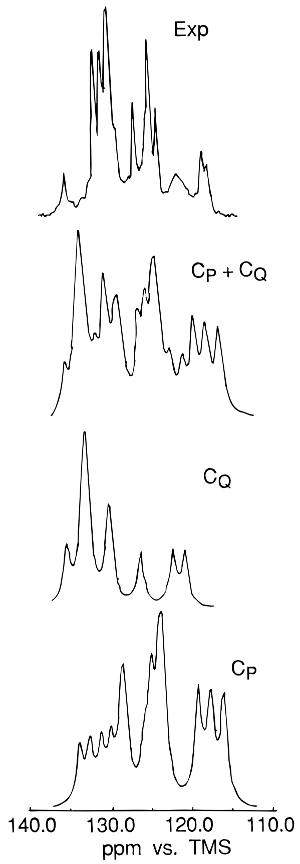


Figure 4. Comparison of observed (Exp) and calculated ^{13}C NMR spectra of crystalline c-(PS)$_5$.

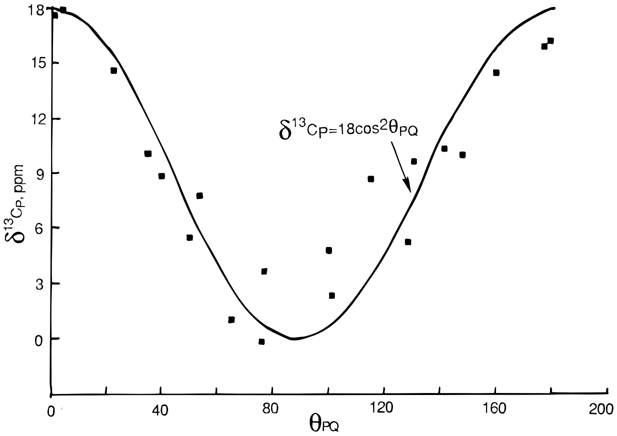


Figure 5. Dependence of nuclear shieldings on dihedral angles θ_{PQ} calculated for the C_P carbons in crystalline c-(PS)$_5$.

In an attempt to understand the ^{13}C NMR spectrum of liquid diphenyl sulfide (DPS; see Figure 7), we have utilized the conformational energy map calculated by

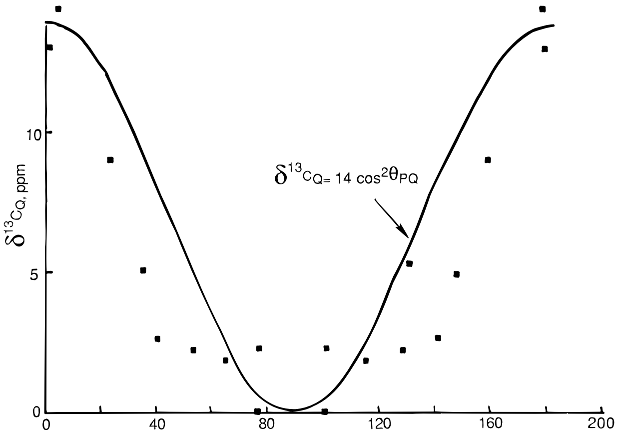


Figure 6. Same as Figure 5 except replace C_P with C_Q.

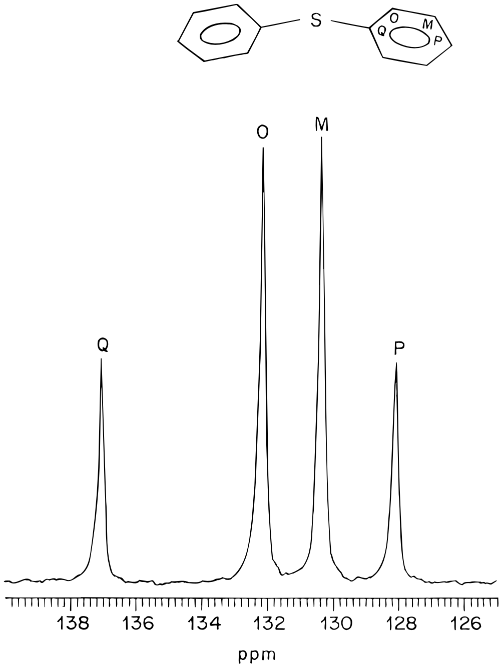


Figure 7. ^{13}C NMR spectrum observed[7] for liquid DPS.

Makowski[22] at the AM1 quantum mechanical level. This was achieved by averaging 18 $\cos^2 \theta_{PQ}$ for C_P carbons and $(0.7)(14 \cos^2 \theta_{PQ})$ for C_Q carbons over the Makowski energy map to obtain the shielding expected for conformationally mobile, liquid DPS. The factor of 0.7 in the expression for C_Q nuclear shieldings (see Figure 6) stems from our observation that the nuclear shieldings calculated for C_Q carbons (see Figure 4) overestimate the overall spread of C_Q resonances observed in c-$(PS)_5$ (see Figure 8).

From Figure 7 we see that the C_P carbons labeled as O in DPS resonate 4.8 ppm upfield from C_Q carbons labeled as Q in DPS liquid. When averaged over Makowski's energy map, the approximate $\cos^2 \theta_{PQ}$ nuclear shielding expressions derived from crystalline c-$(PS)_5$ yield a 4 ppm greater shielding for C_P carbons (O) compared with C_Q carbons (Q), a result in good agreement with that observed in the liquid state ^{13}C NMR spectrum of DPS (see Figure 7).

Further locally dense GIAO nuclear shielding calculations performed on DPS in the $(\phi,\phi) = 45°,45°$; $67.5°,67.5°$; and $90°,90°$ conformations, where $\theta_{PQ} = 45°,135°$; $67.5°,112.5°$; and $90°,90°$, show that M and P carbon nuclear shieldings are conformationally insensitive (see Figure 7). In addition, conformationally insensitive M and P shieldings are 7−10 and 3−8 ppm greater than the conformationally sensitive shieldings calculated for Q and O carbons, respectively (see Figure 7). It would seem fair to suggest that our ability to estimate the nuclear shielding experienced by the C_P and C_Q carbons in the rigid, crystalline c-$(PS)_5$ can be extended to interpret how the ensemble of flexible conformations adopted by liquid DPS are manifested in its ^{13}C NMR spectrum.

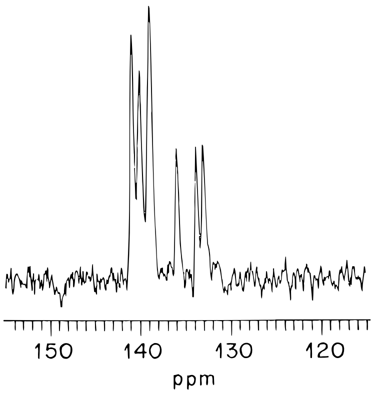


Figure 8. CPMAS/DD ^{13}C NMR spectrum of crystalline c-$(PS)_5$[7] recorded with a 100 μs delay (without spin-locking) in the H-1 channel after the Hartmann−Hahn match.[23] Only C_Q resonances are visible in this spectrum, because C_P nuclei with directly attached protons are rapidly depolarized during the 100 μs delay.

In the solid, DPS apparently crystallizes into an asymmetric conformation, judging from its CPMAS/DD and MAS/DD ^{13}C NMR spectra (See Figure 9). We can see in part b of Figure 9 that two resonances separated by 4 ppm are observed for the Q carbons directly bonded to S. Our previous preliminary assignment of the five visible protonated carbon resonances (O, M, P) (see part c of Figure 9) was O(2), O(1), M(4), O(1), and P(2) from low to high field, with the numbers in parentheses indicating the number of contributing carbons. However, based on our successful estimation of the nuclear shieldings in crystalline c-$(PS)_5$, which are reasonably described by the analytical expressions C_P (shielding in ppm) = 18 $\cos^2 \theta_{PQ}$ and C_Q (shielding in ppm) = 10 $\cos^2 \theta_{PQ}$, we now assume that solid DPS can only evidence at most two separate resonances for both O and Q carbons and single resonances for M and P carbons.

In agreement with the liquid state spectrum (see Figure 7) and the conformational insensitivity of nuclear shieldings estimated for the M and P carbons, the most prominent peak at 132.4 ppm and the most shielded peak at 127.5 ppm in part c of Figure 9 are assigned to the M and P carbons, respectively. Resonances at 141 and 137 ppm are assigned to the Q carbons, O carbon resonances occur at ca. 136 and ca. 130 ppm, and the least shielded Q carbon and most shielded O carbon are separated by ca. 10 ppm.

Makowski's conformational energy map was searched in 10° increments for both C_Q−S bond rotation angles, and nuclear shieldings for Q and O carbons were estimated from the analytical $\cos^2 \theta_{PQ}$ expressions. Only the following asymmetric DPS conformer $\phi_1,\phi_2 = 10°,40°$ or $40°,10°$, with $\phi_1,\phi_2 = 0°,0°$ corresponding to coplanar phenyl rings, yielded nuclear shieldings which closely match the experimental pattern (see Figure 9c) outlined above. This DPS conformer with $\phi_1,\phi_2 = 10°,40°$ or $40°,10°$ has an AM1 energy only 0.7 kcal/mol above the minimum energy conformer $\phi_1,\phi_2 = 35°,35°$ found by Makowski.

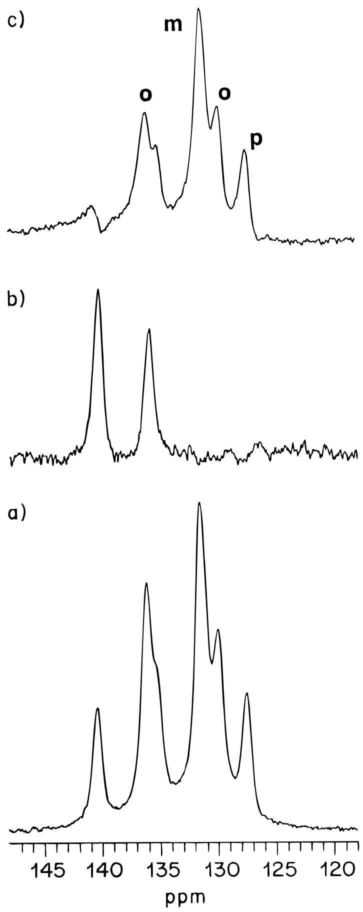


Figure 9. ^{13}C NMR spectra of crystalline DPS.[7] (a) Quantitative MAS/DD spectrum obtained with a 420 s delay between coupling pulses. (b) CPMAS/DD spectrum recorded with a 100 μs delay (without spin-locking) in the H-1 channel after the Hartmann−Hahn match.[23] (c) Difference spectrum [(a) − (b)] showing only protonated carbon resonances.

On the basis of the foregoing analysis, we suggest that DPS crystallizes in the asymmetric conformation with $\phi_1,\phi_2 = \phi_1,\phi_2 = 10°,40°$.

We believe it is apparent that an ability to reasonably estimate the nuclear shieldings experienced by the constituent carbon atoms belonging to conformationally flexible molecules including polymers can provide a powerful means to understand both their ^{13}C NMR spectra and their conformations, regardless of whether or not their conformations are rigid or rapidly interconverting on the NMR time scale of MHz.

Let us return to the origin of the ca. 5 ppm splitting observed[4] for the protonated carbons in crystalline PDMPO and the single resonance observed for the protonated carbons in PPS,[7] despite their identical crystalline conformations.[2,3,5,6] We have already mentioned that the nuclear shieldings calculated for the PDMPO and PPS model compounds MB and MPS were in accord with these observations. However, when nuclear shieldings are calculated for the more appropriate model compounds diphenyl ether (DPE) and DPS, where each is in the $\phi_1,\phi_2, = +45°,-45°$ conformation with C_Q-O-C_Q and C_Q-S-C_Q valence angles (127° and 110°) appropriate[2,3,6] to the crystalline conformations adopted by PDMPO and PPS, 0.4 and 3.6 ppm differences result for the nuclear shieldings of the protonated phenyl ring carbons ortho to the O and S atoms in DPE and DPS, respectively. Though we apparently are able to reasonably estimate the nuclear shieldings in crystalline c-(PS)$_5$ and liquid and crystalline DPS, the same locally dense approach to GIAO quantum mechanical estimation of the nuclear shieldings in the crystalline PDMPO and PPS polymers fails to reveal why in the former polymer the protonated carbons exhibit an ca. 5 ppm inequivalence, while in PPS with the same crystalline conformation the protons are magnetically equivalent within the ca. 1−1.5 ppm experimental resolution.[7]

Let us close our discussion with a brief mention of two recent attempts to estimate the nuclear shieldings expected at the ^{13}C nuclei in synthetic polymers. Born et al.[24] averaged the nuclear shieldings calculated for a tetramer model of polyisobutylene over all conformations and compared them to the observed ^{13}C NMR spectrum of amorphous polyisobutylene. Imashiro and Obara[25] calculated the nuclear shieldings expected for the methine carbons in poly(vinyl alcohol) in the all-trans crystalline backbone conformation by considering the mm, mr, and rr triad stereosequences and all possible OH side chain conformations. The expected shieldings were compared to the solid-state ^{13}C NMR spectrum of crystalline atactic poly(vinyl alcohol). Both of these studies employed ab initio quantum mechanical estimations of ^{13}C nuclear shieldings at a basis set level comparable to that used here.

Each of these studies was successful in reproducing the most prominent aspects of the observed solid-state ^{13}C NMR spectra and both found that the local polymer conformation was principally responsible for the large observed dispersion in ^{13}C chemical shifts (>10 ppm).[26] Taken together with the results reported here, it seems apparent that ab initio quantum mechanical estimation of nuclear shieldings can substantially assist the determination of the structures and conformations of solid polymers via their observation by NMR.

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