Solid state ^{13}C n.m.r. study of poly(*p*-phenylene sulphide) and two model compounds

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Variable temperature, high resolution, solid state ^{13}C n.m.r. spectra are reported for semi-crystalline and amorphous poly(*p*-phenylene sulphide) (PPS), for the crystalline cyclic pentamer of PPS [c-$(PS)_5$], and for crystalline diphenyl sulphide (DPS). Single resonances are observed for both the quaternary (Q) and protonated (P) carbons in crystalline PPS, while only a featureless, broad envelope of resonances is observed for amorphous PPS below its glass transition temperature (T_g) which becomes resolved into single Q and P resonances above T_g. The crystalline, cyclic pentamer c-$(PS)_5$ exhibits multiple resonances (at least six) for both the Q and P carbons which are spread over 8 and 18 ppm, respectively. From the published crystal structures of PPS and c-$(PS)_5$ an attempt is made to understand their ^{13}C n.m.r. spectra in terms of their solid state conformations. In addition, the crystalline conformation of DPS, which has yet to be determined by X-ray diffraction, is discussed based on the ^{13}C n.m.r. spectra observed for this simplest of PPS model compounds.

(Keywords: poly(*p*-phenylene sulphide); ^{13}C n.m.r.; solid state)

INTRODUCTION

Poly(*p*-phenylene sulphide) (PPS) is a high-performance polymer often used as a matrix for fibre-filled composites. Its high temperature and high strength properties[1], its processability and chemical resistance[2], as well as its electrical conductivity upon doping[3,4], have generated increasing interest in its structure. Tabor *et al.*[5] reported a crystal structure for PPS based on X-ray diffraction from stretched fibres, which Lovinger *et al.*[6] have recently confirmed by electron diffraction from PPS single crystals grown from solution and thin molten films. The crystalline conformation of PPS is depicted in *Figure 1*, where all sulphur atoms lie in the same plane and are in the all-*trans* arrangement, while the phenyl rings are successively inclined at ±45° with respect to this plane.

The structurally similar polymers, poly(*p*-phenylene oxide) (PPO) and poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO), both adopt the same crystalline conformation[7,8] illustrated in *Figure 1* for PPS. Schaefer and Stejskal[9] reported the high resolution ^{13}C n.m.r. spectrum of solid PDMPO, where they noted that two resonances were observed for the protonated carbons (P). They attributed this splitting to the non-equivalent environments of the protonated carbons produced by the nonlinear C–O–C bonds. The P carbons become equivalent only when the phenyl rings are rotated 90° out of the plane of the oxygen atoms or when the phenyl rings are able to rotate rapidly. Neither occurs in PDMPO crystals, thus the doubling of the P resonances.

Because PPS adopts the same crystalline conformation as PDMPO, we also expect to see a doubling of P resonances in its high resolution, solid state ^{13}C n.m.r. spectrum. However, previously published solid state spectra of PPS[10-12] exhibit single resonances for both the P and quaternary (Q) carbons. It was the purpose of the present study to understand why different high resolution, solid state ^{13}C n.m.r. spectra are observed for PDMPO[9] and PPS[10-12] though both polymers adopt the same crystalline conformation[5,7,8].

Because the C–S bonds in PPS are substantially longer than the C–O bonds in PDMPO (1.78 *versus* 1.36 Å), the phenyl rings in PPS may be more mobile than those in PDMPO even in their crystalline domains. Mobile phenyl rings could lead to the observation of single resonances for the P carbons in PPS. A variable temperature, high resolution, solid state ^{13}C n.m.r. study might serve to determine the mobility of the phenyl rings in crystalline PPS.

The long C–S bonds in PPS might also remove P and Q carbons that are separated by three bonds (see *Figure 1*) far enough to eliminate or severely reduce the dependence[13] of their ^{13}C chemical shifts upon the conformation of the central C–S bond connecting them. The cyclic pentameter of PPS[c-$(PS)_5$][14,15] crystallizes[16] in a conformation where the relative orientations of phenyl ring pairs bonded to common sulphur atoms are significantly different for all five pairs and are also different from the orientation of phenyl rings in crystalline PPS[5]. Observation of high resolution, solid state ^{13}C n.m.r. spectra of the PPS oligomer c-$(PS)_5$ should indicate whether or not the resonances of the phenyl ring carbons in PPS are expected to be sensitive to its solid state conformation. Although the crystal structure of diphenyl sulphide (DPS) is unknown, it was hoped that observation of its ^{13}C n.m.r. spectra and their comparison to the spectra of PPS and c-$(PS)_5$ would suggest a possible crystalline conformation.

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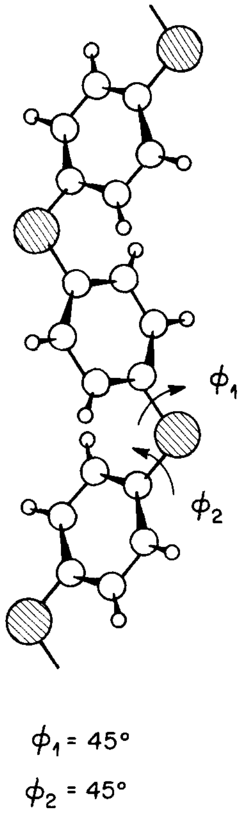

Figure 1 Schematic drawing of the crystalline conformation of PPS[5]

EXPERIMENTAL

The PPS sample studied here was a Phillips Petroleum Ryton VI powder. Several hundred milligrams of the PPS cyclic pentameter, c-$(PS)_5$, were isolated[15] from PPS by methylene chloride extraction. DPS was obtained from Aldrich.

High resolution, solid state ^{13}C n.m.r. measurements were performed on a Varian XL-200 spectrometer operating at a static magnetic field strength of 4.7 T with a ^{13}C resonance frequency of 50.3 MHz. A variable temperature, solids probe from Doty Scientific was used to spin samples at the magic angle (MAS) at speeds of 4–5 kHz. The temperature was varied from −80 to 135°C by use of a cooled or heated N_2 flow, and controlled within ±1°C with a standard Varian temperature control unit. Samples were packed in aluminium oxide rotors with Kel-F[poly(chlorotrifluoroethylene)] end caps for temperatures below 60°C and with Vespel (polyimide) end caps for higher temperatures. Radio frequency field strengths of 45–80 kHz were used for dipolar decoupling (DD) of the ^1H spins, with a decoupling period of 200 ms. The optimal cross-polarization (CP) time was found to be 5 ms at room temperature, and this value was employed at all temperatures. Spectra were recorded with CP(CPMAS/DD) and without CP(MAS/DD), where the delay between decoupling pulses was 1–5 s unless stated otherwise. All spectra were referenced[17] to the resonance of poly(oxymethylene) (POM, 89.1 ppm from TMS) that was recorded externally.

As a means to discriminate between the resonances of protonated (P) and quaternary (Q) carbons, dipolar-dephasing experiments were conducted according to the procedure of Opella and Frey[18]. By applying a 100 μs delay without spin-locking in the ^1H channel after the Hartmann–Hahn match, protonated carbons are relaxed and their signal intensities significantly attenuated compared to the quaternary carbons which possess no efficient pathway for relaxation and therefore show no diminution in signal intensity.

Spin-lattice relaxation times, T_1, were measured under the CP condition by application of the pulse sequence developed by Torchia[19]. The T_1 data were analysed by a nonlinear, least-squares method.

RESULTS AND DISCUSSION

Figure 2 presents the CPMAS/DD ^{13}C n.m.r. spectra of PPS recorded at room temperature with and without the application of a 100 μs dipolar dephasing delay. The spectra in *Figure 2* are similar to those previously reported[10–12] for PPS and serve to confirm the assignment of observed resonances to Q (downfield) and P (upfield) carbons. CPMAS/DD spectra recorded with short contact times (<0.3 ms) only exhibited the P resonance as expected, because of its directly bonded proton.

The MAS/DD ^{13}C n.m.r. spectrum of PPS is presented in *Figure 3a* and is compared to the CPMAS/DD spectrum of a PPS sample quenched from the melt into ice water. Both spectra were recorded at room temperature and are much broader than the CPMAS/DD spectrum of the virgin, semi-crystalline PPS sample presented in *Figure 2a*. CPMAS/DD and MAS/DD ^{13}C n.m.r. spectra recorded for PPS at 135°C are presented in *Figure 4*. Note that at 135°C, which is well above the T_g of amorphous PPS, the MAS/DD spectrum in *Figure 4b* is

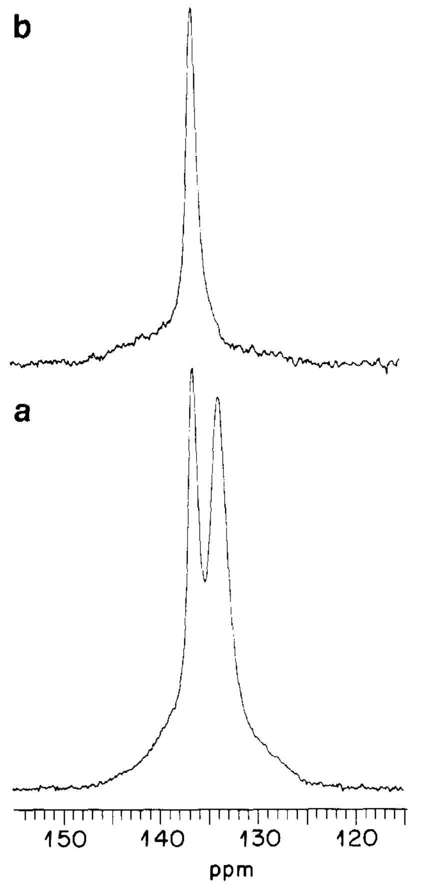

Figure 2 (a) CPMAS/DD ^{13}C n.m.r. spectrum of PPS recorded at room temperature. (b) Same as (a) except with a 100 μs delay (without spin-locking) in the ^1H channel after the Hartmann–Hahn match[18]

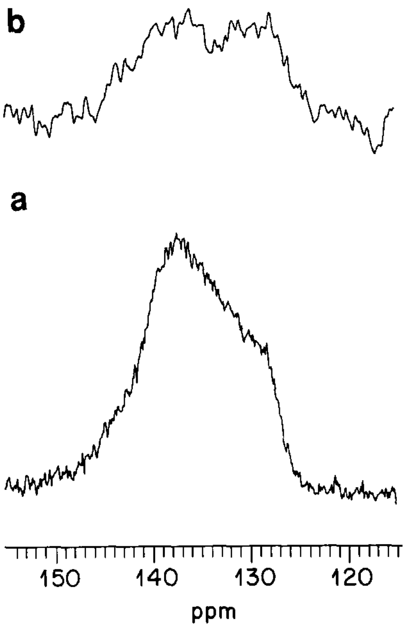

Figure 3 (a) MAS/DD ^{13}C n.m.r. spectrum of PPS recorded at room temperature. (b) CPMAS/DD ^{13}C n.m.r. spectrum of PPS recorded at room temperature after quenching into ice water from the melt

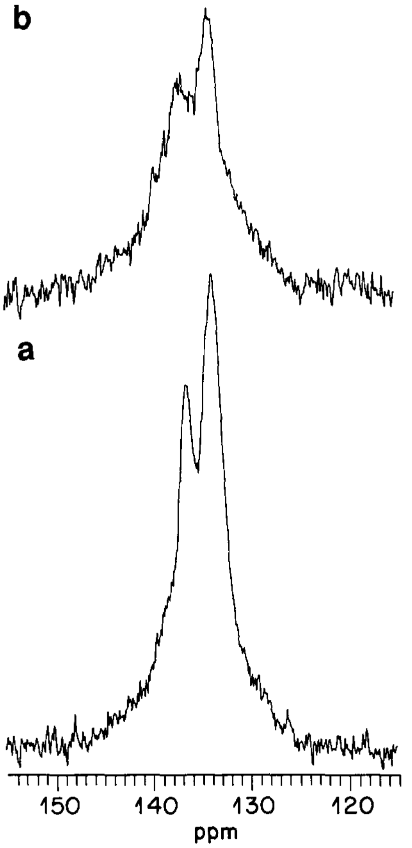

Figure 4 (a) CPMAS/DD ^{13}C n.m.r. spectrum of PPS recorded at 135°C; (b) MAS/DD ^{13}C n.m.r. spectrum of PPS recorded at 135°C

much better resolved than the spectra of amorphous PPS recorded well below T_g at room temperature (see *Figure 3*). Both the P and Q resonances of amorphous PPS resonate *c.* 0.5–1.0 ppm downfield from the crystalline peaks (compare *Figure 4a* and *b*).

Within the resolution of the CPMAS/DD spectra (*Figures 2a* and *4a*) observed for PPS (*c.* 1.5–2.0 ppm for both P and Q resonances), only single peaks are observed for both phenyl ring carbon types. As can be seen in the Newman projection of the PPS crystalline conformation drawn in *Figure 5a*, the dihedral angles between C_Q and C_P's are $\theta_1 = 45°$ and $\theta_2 = 135°$. Based on the conformationally sensitive γ-effect[13] on ^{13}C chemical shifts and the CPMAS/DD spectrum observed for PDMPO[9], we would expect to see two resonances for the P carbons separated by several parts per million, with the most upfield peak corresponding to the C_P carbons separated from C_Q by 45° dihedral angles.

Figure 6 presents the CPMAS/DD ^{13}C n.m.r. spectra recorded without and with dipolar dephasing at room temperature for c-$(PS)_5$. At least six distinct resonances

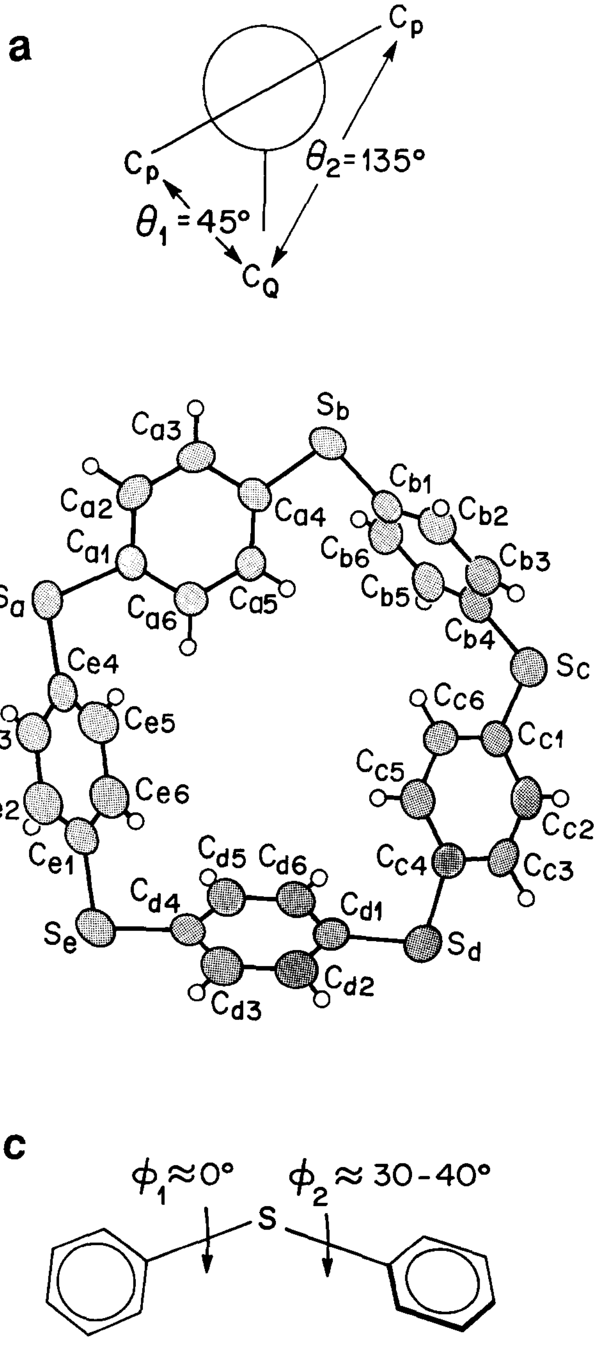

Figure 5 (a) Newman projection along the C_Q–S bond of the crystalline conformation of PPS[5]. (b) Crystalline conformation of c-$(PS)_5$ [16]. (c) Crystalline conformation of DPS suggested by the solid state ^{13}C n.m.r. spectra recorded in the present study

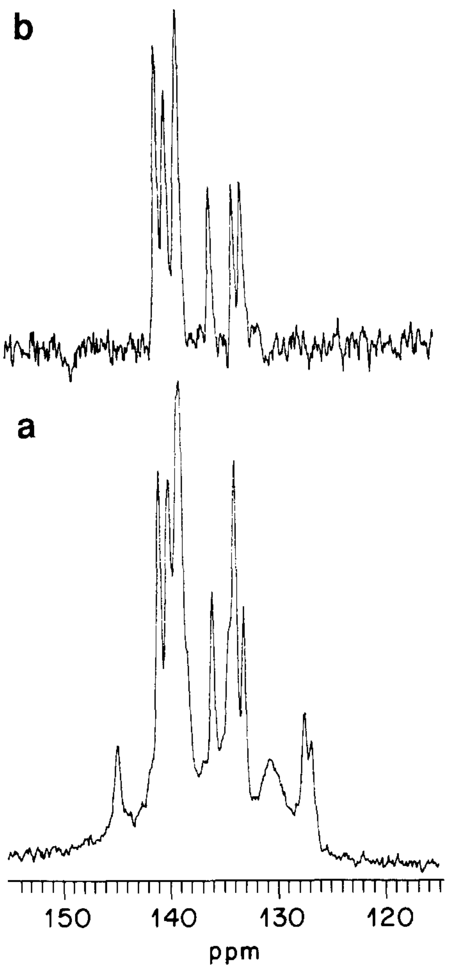

Figure 6 (a) CPMAS/DD ^{13}C n.m.r. spectrum recorded for c-(PS)$_5$ at room temperature. (b) CPMASS/DD ^{13}C n.m.r. spectrum recorded at room temperature for c-(PS)$_5$ with a 100 μs delay (without spin-locking) in the ^{1}H channel after the Hartmann–Hahn match[18]

Table 1 Dihedral angles (θ_{PQ}) between the P and Q ring carbons in crystalline c-(PS)$_5$ (ref. 16)

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	c_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 5b* for the labelling of atoms in c-(PS)$_5$

are observed for both carbon types with an overall spread of 8 ppm for the Q resonances and 18 ppm for the P resonances. *Table 1* presents the dihedral angles between C_P and C_Q carbons observed[16] in the crystal structure of c(PS)$_5$ (see *Figure 5b*). Note that the dihedral angles nearly span the full range from $\theta_{PQ} = 0°$ to 180°, i.e., from the *cis* (0°) to the *trans* (180°) arrangement of C_P and C_Q. 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, then the difference in shielding between a *cis* ($\theta_{PQ} = 0°$) and a *trans* ($\theta_{PQ} = 180°$) arrangement of C_P and C_Q must be 8 and 18 ppm for the Q and P carbons, respectively.

A *cis* arrangement of methyl and protonated ring carbons in solid di- and tri-methoxy benzenes produces[20–23] a 6 ppm shielding relative to their *trans* arrangement. This strongly suggests that the 18 ppm spread in C_P chemical shifts observed for c-(PS)$_5$ is not exclusively a consequence of its crystalline conformation. Another likely contributor to the dispersion of C_P resonances in c-(PS)$_5$ is the variety of C_P–C_Q–S valence angles observed in the X-ray structure. *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 very asymmetric (115.6°, 125.6°). In addition the C_Q–S–C_Q valence angles vary from 100.1° to 104.0° and may be expected to contribute to the dispersion of resonances observed for C_Q.

In *Figure 7* the liquid state ^{13}C n.m.r. spectrum of DPS recorded at room temperature in the Doty solids probe without CP and high power ^{1}H dipolar decoupling and at low spinning speed (< 1 kHz) is displayed. Assignment of resonances is based on the ^{13}C n.m.r. solution spectra reported[24] for phenylthiol and methylphenylsulphide. Solid state ^{13}C n.m.r. spectra observed for DPS at −60°C are presented in *Figure 8*. The spectrum in *Figure 8a* was recorded without CP and with a 420 s delay between decoupling pulses, which is sufficient[25] (*c*. 3 T_1, see *Table 3*) to produce a quantitative spectrum. *Figure 8b* shows the CPMAS/DD spectrum of solid DPS recorded with dipolar dephasing which suppresses the protonated carbon resonances. In *Figure 8c* a difference spectrum (the difference between the spectra in *Figure 8a* and *b*) shows only the resonances of the protonated carbons C_P. The assignment of *o*, *m*, and *p*-C_P resonances is based on their expected 2:2:1 intensity ratios and by comparison to the liquid state spectrum shown in *Figure 7*.

The *m* and *p* resonances are singlets, because the crystalline conformation of DPS is not expected to significantly influence their ^{13}C chemical shifts. On the other hand, the *o*-C_P carbon manifests a resonance doublet centred at 135.5 ppm with a 2:1 ratio of intensities

Table 2 C_P–C_Q–S valence angles in crystalline c-(PS)$_5$ (ref. 16)

(P	Q	X)[a]	$<C_P–C_Q–S_X$
a_2	a_1	a	116.1
a_6	a_1	a	124.4
a_3	a_4	b	115.6
a_5	a_4	b	125.6
b_2	b_1	b	118.9
b_6	b_1	b	121.4
b_3	b_4	c	119.5
b_5	b_4	c	120.9
c_2	c_1	c	116.9
c_6	c_1	c	124.3
c_3	c_4	d	118.7
c_5	c_4	d	123.0
d_2	d_1	d	118.1
d_6	d_1	d	122.3
d_3	d_4	e	121.1
d_5	d_4	e	119.5
e_2	e_1	e	120.2
e_6	e_1	e	120.8
e_3	e_4	a	117.6
e_5	e_4	a	122.9

[a] See *Figure 5b* for atom numbering

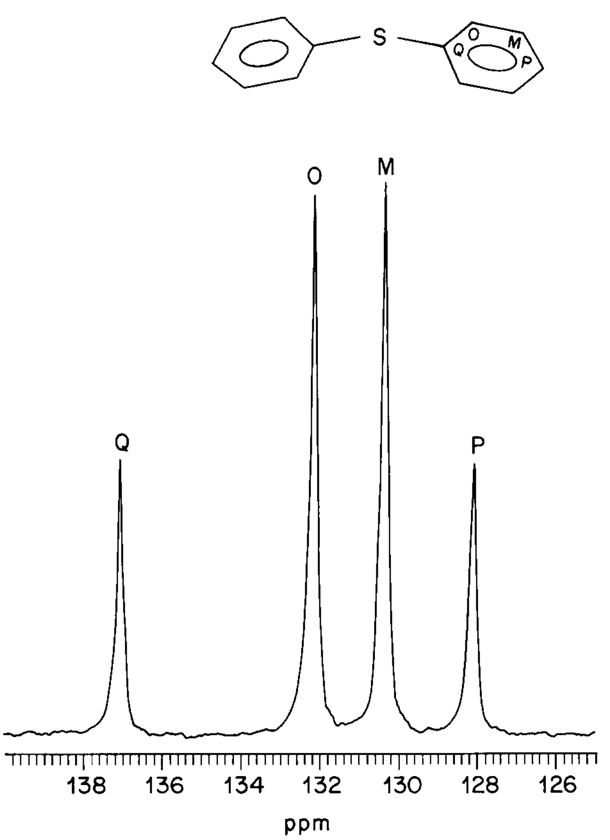

Figure 7 MAS ^{13}C n.m.r. spectrum of DPS in the liquid state recorded at room temperature

and a singlet resonance *c.* 6 ppm upfield at 129.9 ppm corresponding in intensity to a single o-C_P carbon. This pattern of o-C_P resonances may be used to characterize the crystalline conformation of DPS, which has yet to be determined by X-ray diffraction.

If the relative orientations of both phenyl rings with respect to the C_Q–S–C_Q plane were identical or closely similar, then we would expect to observe either a single resonance or a doublet of equal intensities for the o-C_P carbons. A single resonance might result if both rings were perpendicular to the C_Q–S–C_Q plane ($\theta_1 = \theta_2 = 90°$ in *Figure 5a*), though this conformation is not energetically likely[26–30]. If both phenyl rings were similarly oriented with respect to the C_Q–S–C_Q plane with $\theta_1 = \theta_2 \neq 90°$ (see *Figure 5a*), then we might expect to observe a resonance doublet with equal intensities. The observed 2:1:1 triplet of o-C_P resonances permits us to conclude that in the DPS crystal the relative orientation of both phenyl rings with respect to the C_Q–S–C_Q plane are different from each other. This conclusion is further strengthened by the C_Q resonance doublet of equal intensities observed to be split by *c.* 4 ppm (see *Figure 8b*).

A DPS conformation which is consistent with the observed pattern of C_Q and o-C_P resonances is drawn in *Figure 5c*. One phenyl ring is nearly coplanar with C_Q–S–C_Q ($\phi_1 = 0°$), while the other phenyl ring is rotated ($\phi_2 = 30$–$40°$) out of this plane. The dihedral angles between o-C_P and C_Q for these two distinct phenyl ring orientations are $\theta_1 = 0°$, $\theta_2 = 180°$ and $\theta_1 = 30$–$40°$, $\theta_2 = 140$–$150°$, respectively. The least shielded resonances at 136.1 ppm would correspond to the 2 o-C_P carbons with $\theta_2 = 140$–$150°$ and 180°. The resonance shielded by *c.* 1 ppm at 135.1 ppm would correspond to the single o-C_P carbon with $\theta_1 = 30$–$40°$. The most shielded resonance at 129.9 ppm could be assigned to the o-C_P carbon in the *cis* arrangement ($\theta_1 = 0°$) with C_Q. In addition the resonance doublet observed for C_Q carbons and their separation (*c.* 4 ppm) are also consistent with $\theta_1 = 30$–$40°$ and 0° as proposed here for crystalline DPS.

X-ray diffraction studies have been reported for several other phenylene mono- and disulphides. Di-*p*-tolyl sulphide[31] and di-*p*-bromophenyl sulphide[32] adopt symmetric conformers with $\phi_1, \phi_2 = \pm 34°$ and $\pm 40°$, respectively. Bis(4-mercaptophenyl) sulphide[33] and 1,4-bis(phenylthio) benzene[34], on the other hand, assume asymmetric conformations in their crystals with ϕ_1, $\phi_2 =$ 4.2°, 62.2° and 14.9°, 59.2°, respectively. The asymmetric conformer proposed here for crystalline DPS (see *Figure 5c*) based on solid state ^{13}C n.m.r. results does not differ appreciably from the asymmetric crystalline conformations of the latter two mono- and disulphides.

The superior resolution of the DPS spectra (*Figure 8*) compared to the spectra recorded for PPS (*Figures 2–4*) enables us to resolve the o-C_P resonances corresponding to $\theta_1 = 30$–$40°$ and $\theta_2 = 140$–$150°$ and 180°, which are separated by only 1 ppm, while the C_P resonances

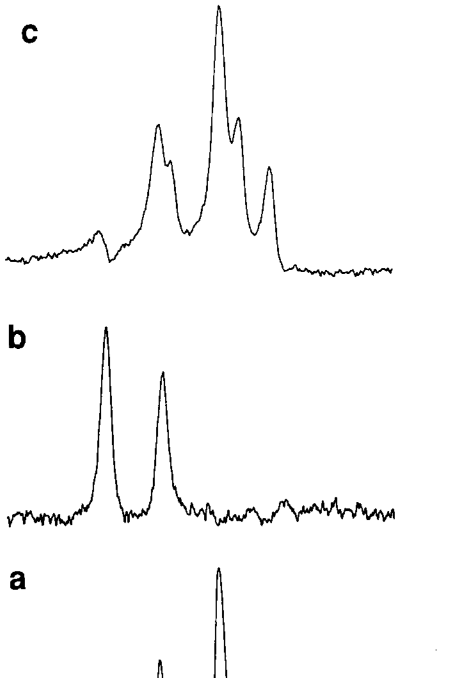

Figure 8 (a) MAS/DD ^{13}C n.m.r. spectrum of DPS recorded at −60°C with a 420 s delay between decoupling pulses. (b) CPMAS/DD ^{13}C n.m.r. spectrum of DPS recorded at −60°C with a 100 μs delay (without spin-locking) in the ^1H channel after the Hartmann–Hahn match[18]. (c) The difference spectrum [(a)–(b)] showing only protonated carbon resonances

Table 3 Spin-lattice relaxation times, T_1(s), measured for PPS, c-$(PS)_5$, and DPS

Compound	T_1 (s)	
	C_Q	C_P
PPS	532	486
c-$(PS)_5$	>400	>400
DPS	167	150(*o*)
		138(*m*)
	150	135(*o*)
		137(*p*)

corresponding to $\theta_1 = 45°$ and $\theta_2 = 135°$ in crystalline PPS remain unresolved due to the *c.* 2 ppm line width of the C_P resonance. Shaefer and Stejskal[9] were able to resolve the splitting of C_P resonances in solid PDMPO, which assumes the same crystalline conformation[5-8] as PPS. This implies that the short C–O bonds (*c.* 1.4 Å) in PDMPO lead to a greater conformational sensitivity of ^{13}C chemical shifts than do the longer C–S bonds (*c.* 1.8 Å) in PPS.

Table 3 presents the results of spin-lattice relaxation times, T_1, measured for PPS, c-$(PS)_5$, and crystalline DPS. Note that both the quaternary and protonated carbons in each sample have T_1 values on the order of several minutes. Clearly the phenyl rings in each of the different crystalline environments provided by these three compounds are restricted in their motions. Rapid 180° ring flips are absent, and small amplitude librations of the phenyl rings may or may not be occurring. It is apparent that rapid rotation of phenyl rings is not the cause of observing single P and Q resonances in the solid state ^{13}C n.m.r. spectra of PPS.

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