

# Intramolecular motions in crystalline phosphonium salts studied by $^{31}\text{P}$ and $^{13}\text{C}$ CP-MAS NMR spectroscopy



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Three homologous trimethylphosphonium bromides with benzyl (1), 2-phenylethyl (2) and 3-phenylpropyl (3) groups were synthesised and their internal conformational motions were examined by solid-state NMR techniques. For compounds 2 and 3 a combination of dynamic line shape changes and  $T_{1\rho}$  measurements of  $^{13}\text{C}$  and  $^{31}\text{P}$  nuclei allow the activation parameters for trimethylphosphonium group rotation in the crystalline solid to be determined. There is excellent agreement between the three independent but complementary NMR methods on the rates of rotation and the activation parameters for the rotation processes. In 1 the rate of rotation of the trimethylphosphonium group is too rapid to be measured.

## Introduction

The importance of understanding molecular motions in crystalline solids has long been realised and was explicitly addressed as long ago as 1973 when Paul and Curtin pointed out that the first step in many solid state chemical reactions should involve molecular loosening. They showed examples where substantial molecular motion was needed for solid state reactions to occur.<sup>1</sup>

Despite this, there is still a belief amongst some chemists, that molecules in solids are fairly firmly held in place by their neighbours in the crystal lattice, a view that arises partly from the static pictures of molecular structures frequently shown by crystallographers. This idea was elegantly expressed by Gavezzotti and Simonetta in 1982:<sup>2</sup> 'A common view among chemists, and even crystallographers, is that a molecular crystal is made up of frozen chemical entities that can at most undergo very small translational and vibrational motions. This is because most of the solid state investigation techniques, as well as theoretical models for the interpretation of their results, see the molecules in such a way.' and this view is still widely held even today. Gavezzotti and Simonetta continued by suggesting that there was reason to suspect that the number of cases of large amplitude molecular motion in molecular crystals '... might be higher than is actually reported, given the fact that many investigators regard large molecular motions in crystals as an unlikely nuisance.' Recent work that we and others have reported demonstrates that, as Gavezzotti and Simonetta suggested, large amplitude molecular motions are in fact extremely common in solids. Many modern chemists now recognise that this is the norm and not the exception.

Although molecular motions in solids may be studied in appropriate cases by examination of anisotropic displacement parameters obtained from X-ray diffraction measurements, solid-state NMR spectroscopy offers better and more diverse methods for this purpose.<sup>3</sup> Many of the nuclear interactions that are present in solids are averaged out by rapid isotropic molecular tumbling in solution. This gives a much richer menu of NMR methods from which to choose for studying motions in solids compared with the solution state. The two principal solid-state NMR methods are the use of specific  $^2\text{H}$  labelling accompanied by the examination of quadrupolar interactions in static samples to probe the molecular motion and the use of dipolar nuclei (principally  $^{13}\text{C}$ ) in CP-MAS experiments.

Many examples of molecular motion in solids have been studied by  $^2\text{H}$  quadrupolar techniques for which two rate ranges

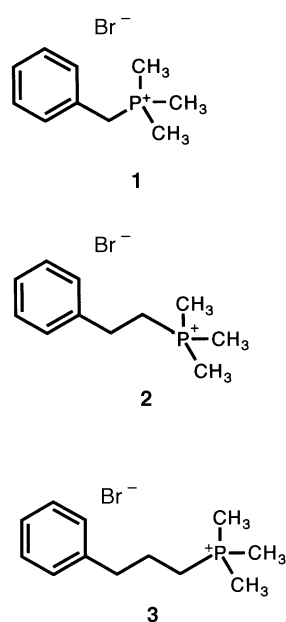
are accessible.<sup>3</sup> For static crystalline samples quadrupolar splitting patterns in the  $^2\text{H}$  spectra of deuteriated molecules arise from an interaction of the nuclear quadrupole with local electric field gradients. The latter are associated with chemical bonds. Motions that produce a directional averaging of the bonds give rise to a spectral frequency change in the rate range *ca.*  $10^3$ – $10^5$   $\text{s}^{-1}$ . Fluctuating electric field gradients also produce spin-lattice relaxation of the  $^2\text{H}$  nucleus and the correlation time for the motion can be inferred if details of the quadrupole interaction are known. Modulation of the electric field gradient in molecular solids is usually produced by rotational molecular or segmental motion. This technique has proved of particular value in chain-like structures, *e.g.* polymers or lipids, where selective deuteration along the chain can characterise the motion of different segments. This approach is most sensitive to motions near to the  $^2\text{H}$  resonance frequency ( $10^7$ – $10^8$   $\text{s}^{-1}$ ).

Equally, many examples are now known where molecular motions in solids have been studied by CP-MAS techniques employing the  $^{13}\text{C}$  nucleus.<sup>3–13</sup> The techniques here include magnetisation transfer or 2D EXSY experiments, dynamic line shape changes and measurements of the relaxation times  $T_1$  and  $T_{1\rho}$ . Magnetisation transfer and 2D EXSY methods give access to lower rates than in solution NMR because of the much longer  $^{13}\text{C}$  spin lattice ( $T_1$ ) relaxation time in solids (from 10 down to  $10^{-3}$   $\text{s}^{-1}$  depending on the case). Dynamic line broadening in solids gives rates in the same range as for solutions from  $10^2$  to  $10^5$   $\text{s}^{-1}$  depending on the chemical shift difference. At higher rates the method of maximum dynamic broadening<sup>14</sup> has been fairly widely employed. This arises when the rate of the incoherent molecular motion is similar to the rate of the coherent precessional frequency of nuclei in the decoupling radio frequency field. This reduces the decoupling efficiency, broadens the lines and gives a single rate constant in the region  $5$ – $10 \times 10^4$   $\text{s}^{-1}$ . The method involving  $T_{1\rho}$  measurements that we have been developing<sup>4–8</sup> gives rates of  $10^4$ – $10^7$   $\text{s}^{-1}$ . As with  $^2\text{H}$  experiments  $T_1$  measurements gives rates *ca.*  $10^7$ – $10^8$   $\text{s}^{-1}$ . Thus, CP-MAS techniques offer a more complete coverage and a wider range of rates (over ten orders of magnitude) than  $^2\text{H}$  techniques. Moreover, no specific isotopic labelling is needed and the motion can be pinpointed to a particular carbon atom, or group of carbon atoms, in the structure.

Some further points need to be made with regard to changes in  $T_{1\rho}$  and with respect to  $T_{1\rho}$  minima (see ref. 4 for a more detailed theory) since these are used extensively in this work.<sup>15</sup>

Cross polarised spectra require a transfer of polarisation from  $^1\text{H}$  to  $^{13}\text{C}$  (or  $^{31}\text{P}$  in this paper) which occurs at a given rate with time constants in the millisecond range. Whilst the polarisation is being transferred it is also being lost from both the  $^1\text{H}$  and  $^{13}\text{C}$  reservoirs by the  $T_{1\rho}$  mechanism which is sensitive to molecular motions at about the precessional frequency of the nuclei in the spin lock field ( $\omega_1$ ). Thus, when the  $T_{1\rho}$  relaxation rate is comparable to the cross polarisation rate ( $T_{1\rho}$ , say  $<2$  ms) there is a reduction in signal intensity in  $^{13}\text{C}$  CP spectra. To determine absolute rates from  $T_{1\rho}$  data requires one to obtain the minimum value of  $T_{1\rho}$  and ( $\omega_1$ ).<sup>4</sup>  $T_{1\rho}$  minima will be deeper for groups with strong dipolar interactions and for those that are close to the motion causing the relaxation. For example, a methyl rotation can cause extremely efficient  $T_{1\rho}$  relaxation for the central carbon, whereas the central carbon in *tert*-butyl group with no directly bound  $^1\text{H}$  is less efficiently relaxed by this mechanism.

The primary purpose of this paper is to show that these CP-MAS NMR techniques, in particular  $T_{1\rho}$  measurements, can be extended to other dipolar nuclei, such as  $^{31}\text{P}$ . Moreover, we demonstrate that rate constants from three complementary but independent NMR techniques,  $^{13}\text{C}$   $T_{1\rho}$  measurements,  $^{31}\text{P}$   $T_{1\rho}$  measurements and  $^{13}\text{C}$  dynamic line shape changes report identical information on the molecular dynamics of a C-P bond rotation process. Because many of our earlier examples were of measurements of the rates of rotation of *tert*-butyl and trimethyl ammonium groups we decided to examine the rotations of the trimethylphosphonium groups in the series



of the compounds (1-3) for the present set of experiments. The  $\text{PMe}_3^+$  group has the same local symmetry as *tert*-butyl or trimethyl ammonium groups ( $C_{3v}$ ) but, because of the larger size of the phosphorous atom, is a larger group. The secondary purpose of this paper is therefore to see then if the larger  $\text{P}^+\text{Me}_3$  group displayed rotational behaviour in the solid similar to that of the smaller groups mentioned above.

## Experimental

### NMR spectra

Solid-state CP-MAS NMR spectra were obtained on a Bruker MSL 500 spectrometer at 125.758 MHz ( $^{13}\text{C}$ ) and 202.458 MHz ( $^{31}\text{P}$ ) using 4 mm o.d. zirconia rotors. The following typical conditions were employed for  $^{13}\text{C}$ : contact time 1 ms, spectral width 30 000 Hz, acquisition time 17.4 ms, spin locking field frequency *ca.* 50 kHz, recycle delay 5 s, spinning speeds 6-8 kHz. Similar conditions but with a reduced spectral width were

used for  $^{31}\text{P}$ . For  $^{13}\text{C}$  spectra between 64 and 400 transients were acquired. For  $^{31}\text{P}$  spectra between 8 and 32 transients were acquired.  $^{13}\text{C}$  chemical shifts were referenced to the  $\text{CH}_2$  resonance in an external adamantane sample at 38.56 ppm. Dipolar dephased [non-quaternary suppressed (NQS)] spectra were obtained by a standard sequence incorporating a 50  $\mu\text{s}$  dipolar dephasing delay.  $^{13}\text{C}$ - $^{31}\text{P}$   $J$  couplings were obtained by resolution enhancement using Gaussian multiplication and are estimated to be accurate to  $\pm 5$  Hz.  $T_{1\rho}$  measurements were performed as described previously using a standard  $T_{1\rho}$  sequence preceded by cross polarisation. Spin lock periods of up to 20 ms were employed with  $^{13}\text{C}$  and  $^{31}\text{P}$  precessional frequencies ( $\omega_1$ ) of *ca.* 50 kHz. Between 16 and 40 transients ( $^{13}\text{C}$ ) and 8 or 16 transients ( $^{31}\text{P}$ ) were acquired for each spin lock delay period. Temperatures in the MAS probe were calibrated as described previously<sup>4</sup> using standard samples with known phase changes run under conditions as close to those of the experimental observations as possible.

Solution state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained from  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  solutions in a 5 mm tube using the high resolution probe in the MSL 500 spectrometer or on either a Bruker AM 300 or a Varian Gemini 200 spectrometer.

Errors in the  $T_{1\rho}$  measurements are estimated to be  $\pm 5\%$ . Errors in the activation parameters quoted in this paper are 95% confidence limits estimated as twice the standard deviation calculated from linear least-square plots.

### Benzyltrimethylphosphonium bromide 1

To benzyl bromide (0.86 g, 5 mmol) in dry ethanol (10 ml) was added trimethylphosphine (0.38 g, 5 mmol) and the solution stirred at room temp. for 2 d. The cloudy mixture was evaporated to a white solid which was washed (light petroleum) and dried under reduced pressure. Yield 1.15 g (93%), mp 226-227 °C (lit.,<sup>16</sup> 222 °C).

### Trimethyl(2-phenylethyl)phosphonium bromide 2

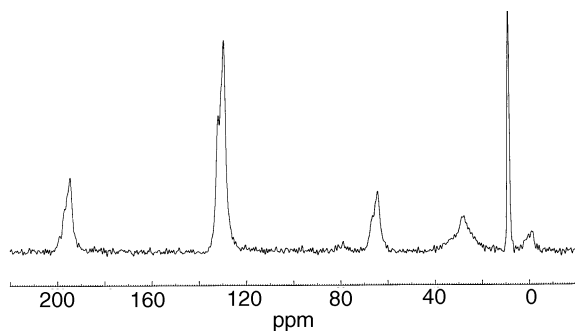
1-Bromo-2-phenylethane (5 mmol) was placed in a glass tube and to this was added 1 M trimethylphosphine in toluene (5 ml, 5 mmol). The tube was then sealed and placed in an oven at 110 °C for 8 h. A white crystalline solid was produced which was recrystallised (ethanol-diethyl ether). Yield 1.08 g, (84%) as a white crystalline solid, mp 168-169 °C;  $\delta_{\text{H}}(\text{D}_2\text{O})$  2.0 (9 H, d,  $J$  10.5, 3 P-CH<sub>3</sub>), 2.7 (2 H, m, P-CH<sub>2</sub>), 3.1 (2 H, m, CH<sub>2</sub>), 7.5 (3 H, m, H-3', 4', 5') and 7.6 (2 H, m,  $J$  7.5, H-2', 6');  $\delta_{\text{C}}(\text{D}_2\text{O})$  8.0 (3 C, d,  $J$  55, 3 P-CH<sub>3</sub>), 24.7 (1 C, d,  $J$  55, P-CH<sub>2</sub>), 27.0 (CH<sub>2</sub>), 127.4 (C-4'), 128.5 (C-3', 5'), 129.4 (C-2', 6') and 139.5 (C-1');  $\text{C}_{11}\text{H}_{18}\text{PBr}$  requires C, 50.59; H, 6.95. Found: C, 50.52; H, 7.18%.

### Trimethyl(3-phenylpropyl)phosphonium bromide 3

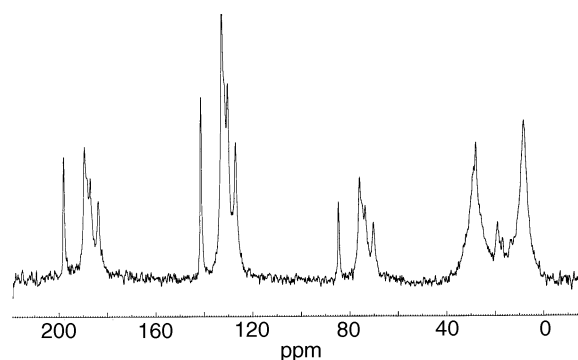
To 1-bromo-3-phenylpropane (2.19 g, 11 mmol) in dry ethanol (10 ml) was added trimethylphosphine (0.74 g, 10 mmol) and the mixture heated to 45 °C for 10 h and stirred at room temp. for 3 d. The mixture was evaporated under reduced pressure and the white solid obtained washed (light petroleum) before recrystallisation (isopropyl alcohol). Yield 1.32 g (48%), mp 145-146 °C.  $\delta_{\text{H}}(\text{CDCl}_3)$  1.9 (2 H, m,  $\text{PhCH}_2\text{CH}_2$ ), 2.15 (9 H, d,  $J$  14, PCH<sub>3</sub>), 2.5 (2 H, m, PCH<sub>2</sub>), 2.8 (2 H, t,  $J$  7.4, PhCH<sub>2</sub>), 7.25 (5 H, m,  $\text{C}_6\text{H}_5$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  9.3 (d,  $J$  54, PCH<sub>3</sub>), 23.6 (d,  $J$  50, PCH<sub>2</sub>), 24.0 (s, PhCH<sub>2</sub>), 36.7 (d,  $J$  17,  $\text{PhCH}_2\text{CH}_2$ ), 127.1, 129.0, 129.3, 140.3 (s,  $\text{C}_6\text{H}_5$ );  $\text{C}_{12}\text{H}_{20}\text{BrP}$  requires C, 52.38; H, 7.32. Found: C, 52.18; H, 7.36%.

### Structure determination of 2

A transparent plate crystal of approximate dimensions 0.5 × 0.25 × 0.12 mm<sup>3</sup> recrystallised from ethanol-diethyl ether was found to be monoclinic. A Rigaku AFC6S diffractometer with graphite monochromator and Cu-K $\alpha$  radiation was used for data collection. A total of 2707 unique reflections ( $h \pm k, \pm l$ ;  $5^\circ < 2\theta < 150.4^\circ$ ) were measured by the  $\omega$ - $2\theta$  technique with a scan range of 0.84 + 0.30 (tan  $\theta$ ) and a scan rate of 8.0° min<sup>-1</sup>



**Fig. 1**  $^{13}\text{C}$  CP-MAS spectrum of benzyltrimethylphosphonium bromide **1** at 125.758 MHz and ambient temperature



**Fig. 2**  $^{13}\text{C}$  CP-MAS spectrum of trimethyl(2-phenylethyl)phosphonium bromide **2** at 125.758 MHz and ambient temperature

(three rescans). An empirical absorption correction was carried out using the program DIFABS and the structure was solved using direct methods (SHELXS86 and DIRDIF92). The hydrogen atoms were generated based on geometric information but their positions were not refined. All important data collection, unit cell and refinement parameters are summarised in Table 3.†

## Discussion

All CP-MAS NMR spectra display spinning side bands displaced from the original resonance by the spinning frequency unless this is larger than the chemical shielding anisotropy. All the spectra in this paper were recorded at speeds around or in excess of 6 kHz and no spinning sidebands were observed for the aliphatic or benzylic resonances but appreciable spinning sidebands were observed for the aromatic resonances. The aromatic signals occur at 120–140 ppm. Their spinning sidebands, which are not marked on the spectra, are symmetrically displaced from them and second-order spinning sidebands are sometimes visible in the aliphatic region. The sidebands never interfered with the observations of dynamic phenomena. The  $^{31}\text{P}$  CP-MAS NMR spectra consisted of single lines and are not shown as Figures.

The trimethylphosphonium bromides **1–3** were synthesised by standard methods from the corresponding alkyl halides and trimethylphosphine. Of the various methods attempted the simplest and most effective is to mix the two components in dry ethanol, warm if necessary, and then stir at room temp. until the reaction is complete (a few days). The salt is then isolated by evaporation and recrystallised. The products either had physical properties in agreement with the literature or gave

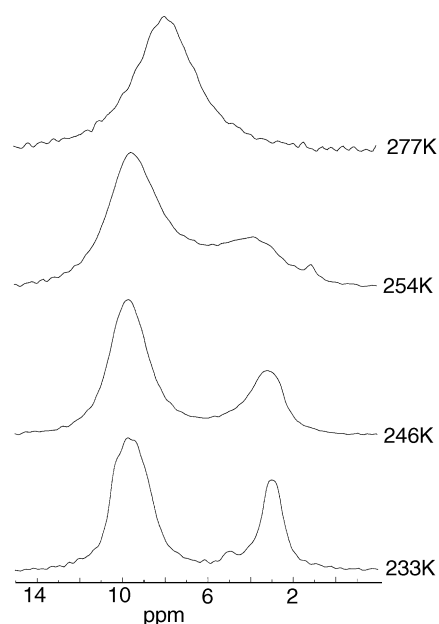
† Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/42.

**Table 1**  $T_{1\rho}$  (ms) and rate ( $\text{s}^{-1}$ ) data for the  $\text{P}^+\text{Me}_3$  group of compound **2** ( $\omega_1 = 48$  kHz)

$T/\text{K}$	$^{13}\text{C}$ $T_{1\rho}$	$k$	$^{31}\text{P}$ $T_{1\rho}$	$k$
364			11.57	$9.4 \times 10^6$
357			7.77	$6.2 \times 10^6$
349	4.84	$5.8 \times 10^6$	5.63	$4.4 \times 10^6$
342	4.30	$5.1 \times 10^6$	4.30	$3.3 \times 10^6$
335	2.01	$2.0 \times 10^6$	3.26	$2.3 \times 10^6$
328	1.52	$7.8 \times 10^5$	2.60	$1.6 \times 10^6$
324			2.51	$1.5 \times 10^6$
320	1.57	$6.7 \times 10^5$	2.22	$7.7 \times 10^5$
317			2.23	$7.7 \times 10^5$
313	1.81	$4.9 \times 10^5$	2.31	$6.6 \times 10^5$
306	1.87	$4.6 \times 10^5$	2.74	$4.5 \times 10^5$
299	2.20	$3.6 \times 10^5$	3.48	$3.2 \times 10^5$
294	4.72	$1.5 \times 10^5$	4.47	$2.4 \times 10^5$

### Line shape data

263	$9.5 \times 10^3$
260	$8.0 \times 10^3$
254	$5.5 \times 10^3$
250	$3.5 \times 10^3$
246	$2.0 \times 10^3$

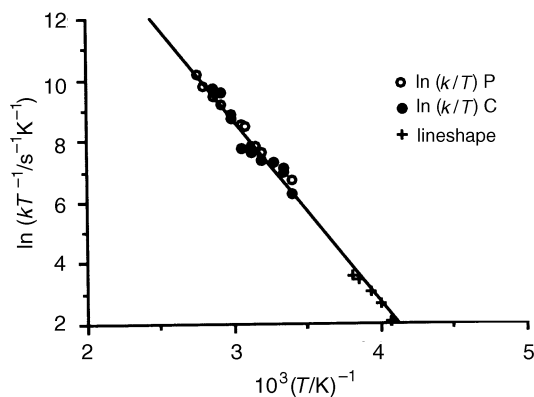


**Fig. 3**  $^{13}\text{C}$  CP-MAS spectrum of trimethyl(2-phenylethyl)phosphonium bromide **2** at 125.758 MHz and varying temperatures

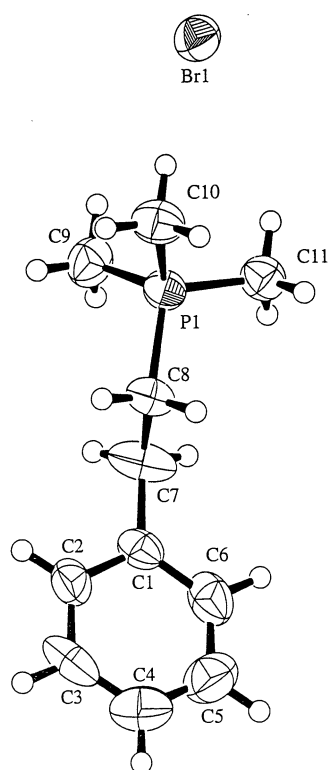
satisfactory microanalyses. Their solution and solid-state NMR spectra were in agreement with the structures.

The room temperature  $^{13}\text{C}$  CP-MAS spectrum of **1** is shown in Fig 1. The spectrum is consistent with rapid rotation of the trimethylphosphonium group shows no changes associated with slowing down of the rate of rotation of the trimethylphosphonium group at temperatures as low as  $-70^\circ\text{C}$  including reductions in signal intensity due to  $T_{1\rho}$  effects and dynamic line broadening. Assuming a chemical shift difference of 2000 Hz this gives a free energy of activation for group rotation considerably below  $30 \text{ kJ mol}^{-1}$ . There may be a coalescence of the phenyl resonances at room temp. arising from a phenyl group rotation but the changes were not sufficiently clear due to the small chemical shift differences involved to merit further investigation.

The ambient temperature  $^{13}\text{C}$  CP-MAS spectrum of **2** is shown in Fig. 2. The phenyl group must be rotating slowly at this temperature as five lines are observed in the phenyl region of the spectrum of which one is of double intensity. The  $\text{P}^+\text{Me}_3$  group is rapidly rotating at this temperature showing a single broad line at 8 ppm. Fig. 3 shows the variable temperature



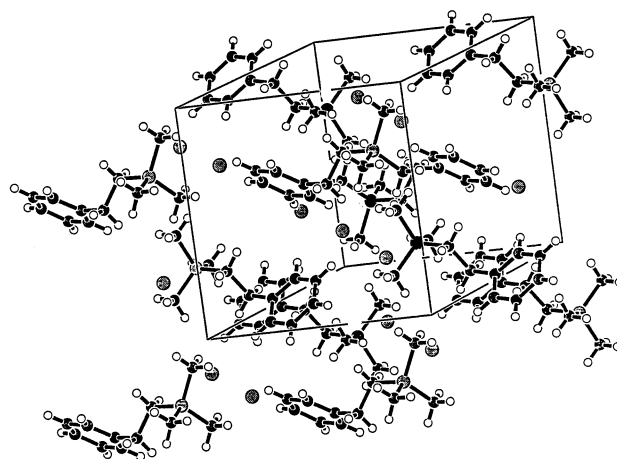
**Fig. 4** Eyring plot showing three complementary sets of data for the trimethylphosphonium group rotation in trimethyl(2-phenylethyl)phosphonium bromide **2**



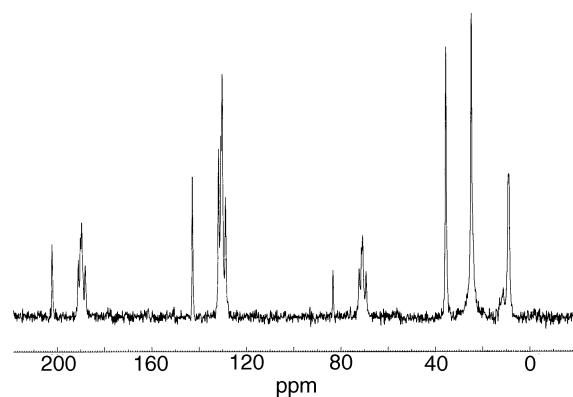
**Fig. 5** ORTEP diagram of the molecular structure of **2**

spectra of the  $P^+Me_3$  group of compound **2**. At low temperatures the methyls are split into a doublet (2 : 1) at 10 and 3 ppm. Resolution enhancement of the low temperature spectrum shows a  $J$  coupling of *ca.* 50 Hz between  $^{13}C$  and  $^{31}P$ . On warming, the peaks coalesce (262 K), sharpen, and proceed through a  $T_{1\rho}$  minimum (*ca.* 320 K). Table 1 gives the  $T_{1\rho}$  and line shape data derived from  $^{13}C$  spectra. Additionally,  $T_{1\rho}$  measurements were performed on the  $^{31}P$  nucleus and this is also presented in Table 1. The data collected from the two nuclei should be complementary and give identical rate data. Rates of rotation derived from the  $T_{1\rho}$  measurements on both nuclei and from line shape calculations at around coalescence are also shown in Table 1 and an Eyring activation plot of the data is given in Fig. 4.

The data from these three independent but complementary NMR methods are satisfyingly consistent, giving further weight to the utility of the  $T_{1\rho}$  method for determining the rate of motions of groups in the solid state. The data give  $\Delta H^\ddagger = 49.4 \pm 2.8$  kJ mol $^{-1}$  and  $\Delta S^\ddagger = 22.8 \pm 8.6$  J K $^{-1}$  mol $^{-1}$ .



**Fig. 6** Packing of molecules of **2** in the unit cell



**Fig. 7**  $^{13}C$  CP-MAS spectrum of trimethyl(3-phenylethyl)phosphonium bromide **3** at 125.758 MHz and ambient temperature

These data would give a free energy of activation for the group rotation of 42.7 kJ mol $^{-1}$  at 293 K (ambient temperature).

The structure of **2** in the solid state was determined by X-ray diffraction (Figs. 5 and 6). The C1, C7, C8, P1 chain is seen to be in an almost linear arrangement, *trans* about the central bond with the plane of the phenyl ring approximately perpendicular to the approximate plane C1, C7, C8, P1. The anisotropic thermal parameters for the three methyl groups show little evidence of having a substantial contribution along the direction of  $PMe_3$  rotation unlike earlier compounds we have examined.<sup>4,5</sup> The phenyl groups are adjacent to each other but with their planes at an angle of approximately 90°. The bromide ion is almost directly on the axis of the C8–P1 bond with distances to the methyls of 383–398 pm. The only other close contact for the P-methyl carbons is 385 pm between C10 and one of the phenyl *meta* carbons.

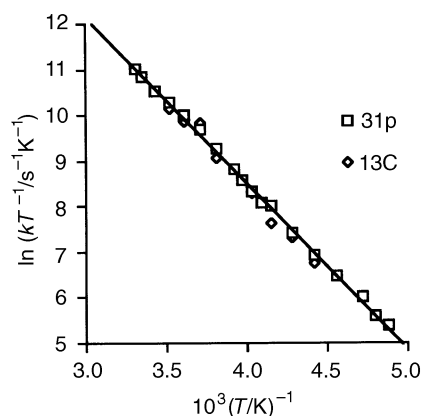
The ambient temperature  $^{13}C$  CP-MAS spectrum of **3** is shown in Fig. 7. Resolution enhancement of the  $PMe_3$  resonance shows a  $^{31}P$ – $^{13}C$  coupling of *ca.* 53. Below ambient temperature there is a reduction in intensity of the  $^{13}C$  spectrum of the methyl groups and the  $^{31}P$  resonance consistent with reduced cross polarisation efficiency due to a reduction in  $T_{1\rho}$ . The coalescence for the  $P^+Me_3$  rotation occurs at temperatures below the lower limit of our current apparatus (<170 K).  $T_{1\rho}$  values and the derived rate constants for rotation are shown in Table 2. Again, there is excellent agreement between the rates obtained for both nuclei and as expected the  $T_{1\rho}$  minima are at the same temperature (*ca.* 248 K) for both nuclei. The Eyring activation plots for both sets of data are shown superimposed in Fig. 8. The  $P^+Me_3$  group in this compound is rotating faster than in **2** and this is reflected in lower energies of activation. The data give  $\Delta H^\ddagger = 32.2 \pm 0.6$  kJ mol $^{-1}$  and

**Table 2**  $T_{1\rho}$  (ms) and rate ( $s^{-1}$ ) data for the  $P^+Me_3$  group of compound **3** ( $\omega_1 = 55$  kHz)

$T/K$	$^{31}P$ $T_{1\rho}$	$^{31}P$ $k$	$^{13}C$ $T_{1\rho}$	$^{13}C$ $k$
205	35.5	$4.54 \times 10^4$		
208	28.6	$5.64 \times 10^4$		
212	18.5	$8.74 \times 10^4$	13.0	$7.69 \times 10^4$
219	11.6	$14.1 \times 10^4$	8.20	$12.4 \times 10^4$
227	7.20	$23.4 \times 10^4$	5.39	$19.2 \times 10^4$
234	4.70	$39.1 \times 10^4$	3.16	$35.1 \times 10^4$
241	3.30	$72.5 \times 10^4$	2.52	$49.9 \times 10^4$
245	3.20	$80.4 \times 10^4$		
248	3.10	$10.4 \times 10^5$	2.03	$10.0 \times 10^5$
252	3.20	$13.3 \times 10^5$		
255	3.50	$17.1 \times 10^5$		
262	4.90	$27.8 \times 10^5$	2.73	$22.6 \times 10^5$
270	7.00	$44.4 \times 10^5$	5.30	$51.0 \times 10^5$
277	9.50	$61.9 \times 10^5$	5.57	$54.2 \times 10^5$
284	12.8	$84.3 \times 10^5$	7.37	$72.6 \times 10^5$
292	16.6	$11.0 \times 10^6$		
299	23.4	$15.5 \times 10^6$		
303	28.0	$18.6 \times 10^6$		

**Table 3** Crystallographic data for **2**

Formula	$C_{12}H_{20}BrP$
Formula mass	261.14
Habit	Monoclinic
Lattice type	$P$
Space group	$P2_1/n$
$Z$	4
$a/\text{\AA}$	10.242(2)
$b/\text{\AA}$	10.380(2)
$c/\text{\AA}$	12.745(1)
$\beta/^\circ$	110.89(1)
$V/\text{\AA}^3$	1265.9(3)
$D_c/\text{g cm}^{-3}$	1.370
$T/^\circ\text{C}$	23
$\mu/\text{cm}^{-1}$	52.74
$\lambda$ (Cu-K $\alpha$ graphic monochromated)/ $\text{\AA}$	1.54178
$R$	0.047
$R_w$	0.039

**Fig. 8** Eyring plot showing two complementary sets of data for the trimethylphosphonium group rotation in trimethyl(2-phenylethyl)-phosphonium bromide **3**

$\Delta S^\ddagger = -6.1 \pm 2.3 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $^{31}\text{P}$ ) and  $30.4 \pm 2.1 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -6.4 \pm 8.6 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $^{13}\text{C}$ ); the larger errors on the  $^{13}\text{C}$  values reflect the poorer signal to noise ratio in the spectra of the less abundant nucleus. Using the  $^{31}\text{P}$  data a free energy of activation for the group rotation of  $34.0 \text{ kJ mol}^{-1}$  at 293 K may be calculated.

## Conclusions

This work has reemphasised the validity and utility of CP-MAS methods for examining molecular dynamics in solids. In particular it has shown that  $T_{1\rho}$  measurements on  $^{31}\text{P}$  can provide information on solid-state molecular dynamics in crystalline organic solids that complement and agree with the information available from  $^{13}\text{C}$  lineshape and  $T_{1\rho}$  measurements. The agreement between the three independent but complementary NMR techniques for measurement of solid-state dynamics is both very satisfactory and highly satisfying.

The enormous variability in activation parameters seen in our earlier studies on ammonium salts<sup>8</sup> is once again apparent in the series, with the free energy of activation for the same process in different compounds varying from less than 30 to 43  $\text{kJ mol}^{-1}$ . The packing of molecules in the solid must be a dominating influence on the energetics of such processes. Although entropies of activation from NMR measurements are notoriously questionable we believe that the difference in these values between **2** ( $\Delta S^\ddagger = -6.1 \pm 2.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and **3** ( $\Delta S^\ddagger = 22.8 \pm 8.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is indeed a reflection of a real difference in the entropies of activation.

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