Further studies of intramolecular motions in crystalline ammonium bromides by CP/MAS NMR

Frank G. Riddell and Martin Rogerson

School of Chemistry, The University of St Andrews, St Andrews, UK KY16 9ST

A series of nine compounds consisting of dimethyl, trimethyl and ethyldimethyl ammonium bromides in which the other alkyl group contains a (2-phenyl)ethyl moiety were synthesised and studied by CP/MAS NMR. The results of dynamic NMR studies on the solids suggest that there is a dramatically wide range of molecular motions occurring in this simple series of compounds. A combination of dynamic line shape analyses and $T_{1\rho}$ measurements reveals the considerable extent of intramolecular group motions including rotations of trimethylammonium, ethyldimethylammonium and phenyl groups. Rates of rotation and activation parameters for these molecular motions are derived where appropriate.

Introduction

The importance in chemistry of intramolecular motions in crystalline organic solids was recognised over two decades ago.[1] However, the full extent of their occurrence is widely underestimated.[2] Few chemists are aware of the extent of such motions apart from segmental motions in systems such as solid polymers, or in plastic crystals or crystalline materials with molecules of high symmetry such as benzene, where rotations of whole molecules occur. Molecules with irregular shapes or strong ionic interactions would not be expected by many chemists, even today, to display large amplitude segmental motions. This view is reinforced by the (static) pictures displayed of the results of X-ray diffraction studies.

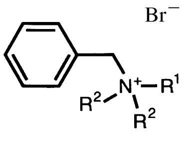
In fact, although molecular motions can be demonstrated by examining the temperature dependence of anisotropic displacement parameters from X-ray diffraction, this is not the most effective method for deriving kinetics and activation parameters. NMR spectroscopy, by contrast, is ideally suited for measurements of molecular dynamics, particularly in solids, where a wide range of methods is available for such investigations.[3] We and others have shown that CP/MAS NMR methods can be used to study intramolecular motions.[3–17] Although ^{13}C CP/MAS NMR methods for this are extremely powerful they seem to be underemployed.

A wide variety of CP/MAS NMR methods for the study of dynamic processes in solids is available.[3] The general rule is that when the frequency of the molecular motion is similar to that of an NMR interaction effects are observable in the spectrum. Rates measurable by dynamic line shape changes are comparable to the chemical shift difference and typically fall into the range 10^2–10^4 s^{-1}. Rates measurable by $T_{1\rho}$ measurements can be made when the rate of the molecular motion is similar to the precessional frequency of the nuclei in the spin locking field, typically 50–100 kHz.[5,14] Such rates typically extend from *ca.* 10^4 to as high as 10^7 s^{-1}. Similar, but not identical, is the method of so called maximum dipolar broadening.[15] This occurs when the rate of the incoherent molecular motion is similar to and so interferes with the coherent precessional frequency of the dipolar (^{1}H) decoupling field. This gives a single rate at the precessional frequency of the ^{1}H nuclei in the decoupling field. It should be noted that, when performing $T_{1\rho}$ measurements, if the ^{13}C spin lock field and the decoupler power are the same as during the Hartman–Hahn condition, maximum dipolar broadening will occur at the same temperature as the $T_{1\rho}$ minimum. Importantly, the derivation of rates of molecular motions from relaxation time measurements is independent of whether there is a coalescence phenomenon possible or not. Thus, in the context of this work, $T_{1\rho}$ measurements will provide activation data for rotations of both the phenyl and trimethylammonium groups that display coalescence phenomena as well as for the dimethylammonium and ethyldimethylammonium groups that do not. The range of rates can equally be extended in the lower limit by magnetisation transfer or 2D CPEXSY measurements where rates comparable with ^{13}C relaxation times are accessible.[18,19] Using such methods we have measured rates as low as 10 sec^{-1}. Thus six orders of magnitude in rates of rotation are, in principle, available for study using these ^{13}C CP/MAS NMR techniques with almost continuous coverage of the range. The range may be extended further by use of T_1 and T_2 measurements.[3]

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. 5 for a more detailed theory) since these are used extensively in this work. Cross polarised spectra require a transfer of polarisation from ^{1}H to ^{13}C 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}H and ^{13}C reservoirs by the $T_{1\rho}$ mechanism. Thus, efficient $T_{1\rho}$ relaxation leads to a reduction in signal intensity in CP spectra. To determine absolute rates from $T_{1\rho}$ data requires one to obtain the minimum value of $T_{1\rho}$ and to know the precessional frequency of the ^{13}C nuclei in the spin locking field (ω_1).[5] $T_{1\rho}$ 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 a *tert*-butyl group with no directly bound ^{1}H is less efficiently relaxed by this mechanism.

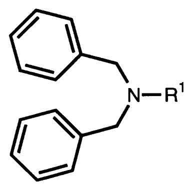
We have recently shown that a remarkably wide range of intramolecular (conformational) motions occurs in the simple series of benzylammonium bromides and benzylamines represented by structures **1** and **2**.[16] The rotations observed in that paper were of alkyl groups attached to a quaternary ammonium centre. It seemed to us reasonable to extend this work to attempt to observe the rotations of the ammonium centre itself in the series of compounds **3**–**5**. The new series is essentially isostructural with the previous series with the nitrogen moved along the chain by one position. The logic behind the design of this series **3**–**5** was similar to that in our previous series.[16] The idea was that the (2-phenyl)ethyl groups would form a static reference frame against which the trialkylammonium group rotations could be observed. In fact phenyl rotations in our 'static reference frame' turned out to be important too.

In the series of compounds **1** and **2** we measured the kinetics



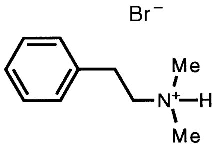
1

R^1= Pr^i,Bu^t, *tert*-amyl
R^2= H, Me, CH$_2$Ph

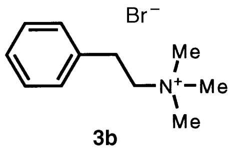


2

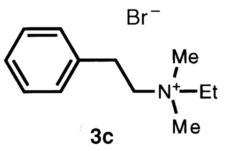
R^1= Pr^i,Bu^t, *tert*-amyl



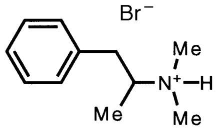
3a



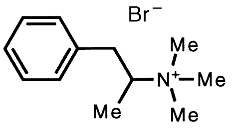
3b



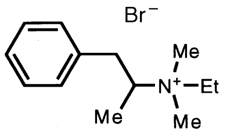
3c



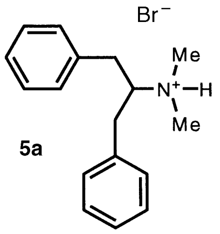
4a



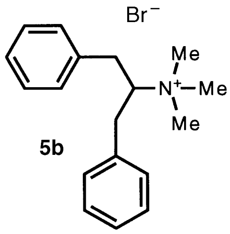
4b



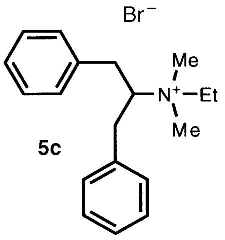
4c



5a



5b



5c

of the rotations of methyl, *tert*-butyl, *tert*-amyl and phenyl groups. We have also observed rotations of trimethylphosphonium groups.[17] By analogy in the current series of compounds **3**–**5** we expected to observe rotations of methyl, trimethylammonium, ethyldimethylammonium and phenyl groups. We demonstrate in this paper, by examining this simple series of compounds, that trialkylammonium group rotations occur in crystalline solids. The results reinforce the fact that there is an enormous variety of large amplitude molecular motions in molecular crystals that contain molecules of irregular shape and they extend the range of compounds in which such motions have been examined by solid-state CP/MAS NMR techniques.

Experimental

Preparation of compounds

Standard procedures were employed scaled up or down as appropriate and are given below:

(*A*) Hydrobromination of an amine. The amine (0.01 mol) was dissolved in ethanol (20 cm^3) and to this was added 48% hydrobromic acid (1.69 g, 0.01 mol). The solvent was removed leaving a white solid which was recrystallised from ethanol–diethyl ether.

(*B*) Alkylation of an amine. The amine (*ca.* 2 g) was dissolved in dichloromethane (2 cm^3). The alkyl bromide was bubbled through the solution to form a white precipitate. This was collected at the pump and recrystallised from ethanol–diethyl ether.

(*C*) Dimethylation of an amine (Eschweiller Clark Reaction). The amine (0.25 mol) was added to 40% aqueous formaldehyde (35 g, 0.5 mol) in water with cooling in ice–water. To this was added 98% formic acid (23.5 g, 0.5 mol) and the solution was then heated under reflux for 6 h. After this time NaOH pellets (10 g, 0.25 mol) were added. The resultant organic layer was separated, dried (anhydrous K_2CO_3) and distilled.

N,*N*-Dimethyl-2-phenylethylamine was prepared from 2-phenylethylamine using method *C*.

Compound **3a** was prepared from *N*,*N*-dimethyl-2-phenylethylamine by method *A*. **3a** was a white crystalline solid, mp 145–146 °C.

Compound **3b** was prepared from *N*,*N*-dimethyl-2-phenylethylamine by method *B*. **3b** was a white crystalline solid, mp 233–234 °C.

Compound **3c** was prepared from *N*,*N*-dimethyl-2-phenylethylamine by method *B*. **3c** was a white crystalline solid, mp 152–153 °C.

To prepare 1-phenyl-2-aminopropane, the oxime of benzylmethyl ketone (10.46 g, 0.07 mol) was dissolved in superdry ethanol and the solution brought to the boil. Heating was stopped and metallic sodium (16.15 g, 0.7 mol) added at such a rate as to maintain vigorous reflux. After the addition of sodium was complete the solution was acidified with dilute aqueous hydrochloric acid, cooled and extracted with diethyl ether. Sodium hydroxide pellets were then added to the aqueous layer until it was basic and an oil had separated. The oil was extracted with diethyl ether, dried (anhydrous K_2CO_3) and the solvent removed. Yield of crude 1-phenyl-2-aminopropane 8.51 g (90%) as a yellow liquid. This was used without further purification.

N,*N*-Dimethyl-2-phenylpropylamine was prepared from crude 1-phenyl-2-aminopropane by method *C*.

Compound **4a** was prepared from *N*,*N*-dimethyl-2-phenylpropylamine by method *A*. **4a** was a white crystalline solid, mp 154–155 °C.

Compound **4b** was prepared from *N*,*N*-dimethyl-2-

Table 1 Analytical data (%) for compounds synthesised

		Carbon		Hydrogen		Nitrogen	
Compound	Formula	Required	Found	Required	Found	Required	Found
3a	$C_{10}H_{16}NBr$	52.18	52.41	7.01	7.03	6.09	6.09
b	$C_{11}H_{18}NBr$	54.11	54.18	7.43	7.59	5.74	5.72
c	$C_{12}H_{20}NBr$	55.82	55.96	7.81	7.97	5.42	5.44
4a	$C_{11}H_{18}NBr$	54.12	54.31	7.43	7.67	5.74	5.74
b	$C_{12}H_{20}NBr$	55.82	55.94	7.81	8.01	5.42	5.50
c	$C_{13}H_{22}NBr$	57.34	57.77	8.15	8.04	5.14	5.15
5a	$C_{17}H_{22}NBr$	63.75	64.19	6.92	7.08	4.37	4.48
b	$C_{18}H_{24}NBr$	64.67	64.88	7.24	7.52	4.19	4.30
c	$C_{19}H_{26}NBr$	65.62	65.65	7.52	8.07	4.02	4.06

phenylpropylamine by method *B*. **4b** was a white crystalline solid, mp 140–141 °C.

Compound **4c** was prepared from *N*,*N*-dimethyl-2-phenylpropylamine by method *B*. **4c** was a white crystalline solid, mp 120–121 °C.

To prepare 1,3-diphenyl-2-aminopropane, the oxime of dibenzyl ketone (6.3 g, 0.044 mol) was dissolved in superdry ethanol and the solution brought to the boil. Heating was stopped and metallic sodium (10.1 g, 0.44 mol) added at such a rate as to maintain vigorous reflux. After the addition of sodium was complete the solution was acidified with dilute aqueous hydrochloric acid, cooled and extracted with diethyl ether. Sodium hydroxide pellets were then added to the aqueous layer until it was basic and an oil had separated. The oil was extracted with diethyl ether, dried (anhydrous K_2CO_3) and the solvent removed. Yield of crude 1,3-diphenyl-2-aminopropane 5.36 g (86%) as a yellow liquid. This was used without further purification.

1,3-Diphenyl-2-(dimethylamino)propane was prepared from 1,3-diphenyl-2-aminopropane by method *C*.

Compound **5a** was prepared from 1,3-diphenyl-2-(dimethylamino)propane by method *A*. **5a** was a white crystalline solid, mp 198–199 °C.

Compound **5b** was prepared from 1,3-diphenyl-2-(dimethylamino)propane by method *B*. **5b** was a white crystalline solid, mp 205–206 °C.

Compound **5c** was prepared from 1,3-diphenyl-2-(dimethylamino)propane by method *B*. **5c** was a white crystalline solid, mp 209–210 °C.

Microanalytical data on compounds **3a**,**b**,**c**; **4a**,**b**,**c** and **5a**,**b**,**c** are recorded in Table 1.

NMR Spectra

Solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker MSL 500 spectrometer at 125.758 MHz using 4 mm o.d. zirconia rotors. The following typical conditions were employed: contact time 1 ms, spectral width 30 000 Hz, acquisition time 17.4 ms, spin locking field frequency *ca.* 60 kHz, recycle delay 5 s, spinning speeds 6–8 kHz. Chemical shifts were referenced to the CH_2 resonance in an external adamantane sample at 38.56 ppm. Dipolar dephased [non quaternary suppressed (NQS)] spectra to aid spectral assignments were obtained by a standard sequence incorporating a 50 μs dipolar dephasing delay. $T_{1\rho}$ 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}C precessional frequencies (ω_1) of *ca.* 60 kHz. Temperatures in the MAS probe were calibrated using standard samples with known phase changes run under conditions as close to those of the experimental observations as possible.[20] Line shape analyses for a three site system were calculated using a computer program kindly supplied by Dr J. E. Anderson. Matching of calculated and observed spectra was done by visual comparison, by measurements of relative heights of peaks and valleys and by measurements of line widths. Solution state ^{1}H and ^{13}C NMR spectra were obtained from $CDCl_3$ or D_2O 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.

Activation parameters were derived from Eyring or Arrhenius plots of the rate data or from plots of $\ln(T_{1\rho})$ *vs.* $1/T$. The theory and details of these methods are discussed in refs. 5 and 7. Errors on the activation parameters quoted in this paper are 95% confidence limits estimated as twice the standard deviation calculated from least-squares linear plots. Errors on the $T_{1\rho}$ values in this paper vary with the signal to noise ratio available from the sample in a reasonable time period. They would typically be *ca.* ±5%.

Results and 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 shift anisotropy. In all the spectra in this paper 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 between 120 and 140 ppm. Their spinning sidebands 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. No examples of residual dipolar coupling between ^{13}C and ^{15}N were observed due to the high magnetic field (11.75 T) employed.

Compounds in the series were prepared as the racemic modifications and this has consequences for the likely number of signals observed.†

The room temperature spectra of compounds **3a**,**b** and **c** are shown in Fig. 1.

The spectrum of compound **3a** shows two *N*-methyls at 43 and 46 ppm due to molecular dissymmetry in the solid. The benzylic CH_2 is at 32 ppm with the *N*-CH_2 at 60 ppm. The ring carbons are located at 130 ppm while the quaternary aromatic carbon is at 137 ppm. There is no change in the relative intensity of the methyl peaks with varying temperature indicating that rotation of the dimethylammonium group is slow. However, at low temperature (263 K) the aromatic ring carbons are represented by four peaks; Fig. 2. As the temperature is increased the inner two peaks, from the four off-rotation axis carbons broaden (292 K), coalesce (299 K) and sharpen dram-

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† If the compound spontaneously resolves giving a racemic mixture, two possibilities need considering. With only one molecule in the asymmetric unit only one set of signals will be observed, but with two independent molecules in the asymmetric unit all lines will be doubled. If on the other hand a racemic compound is formed with both enantiomers present in the solid, two possibilities also need considering. If there is a mirror plane relating the enantiomeric molecules in the solid, only one set of signals will be observed. If there is one molecule of each enatiomer in the asymmetric unit without any symmetry relationship between them, two sets of signals will be observed.

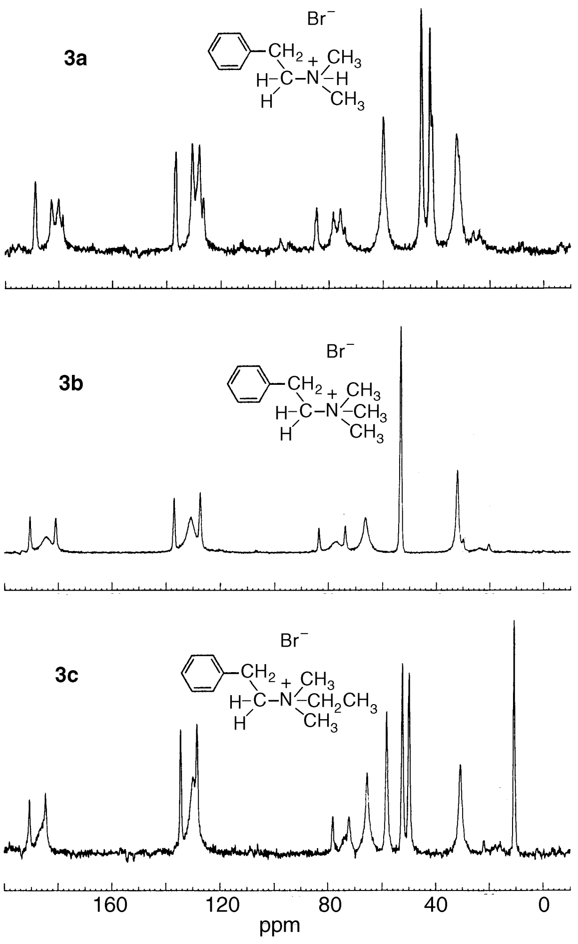

Fig. 1 Ambient temperature ^{13}C CP/MAS NMR spectra of compounds **3a**,**b** and **c** measured at 125.758 MHz

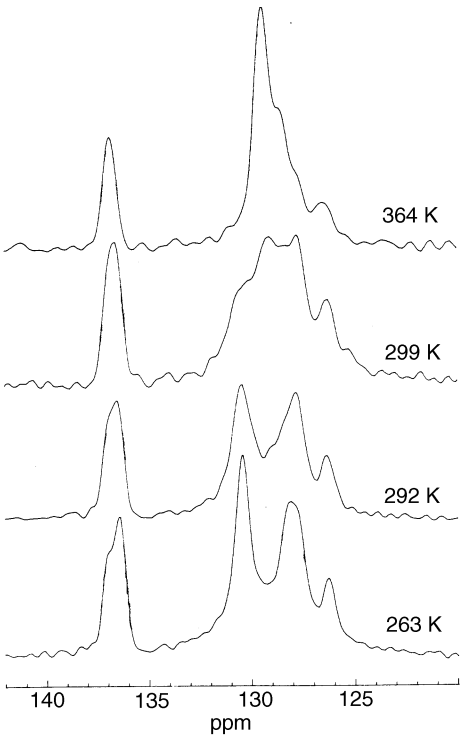

Fig. 2 Variable temperature ^{13}C CP/MAS NMR spectra of the aromatic region in compound **3a**, measured at 125.758 MHz

atically (364 K) into one peak. The on-axis carbons remain unaffected. This phenomenon is indicative of a rapidly rotating phenyl group. The free energy of activation for this phenyl rotation process taken from the coalescence temperature is *ca.* 55 kJ mol^{-1} at 299 K. No $T_{1\rho}$ data were collected.

Table 2 $T_{1\rho}$ and rate data for compound **3b**; (ω_1 = 61 kHz)

	53ppm	130ppm	
T/K	$T_{1\rho}$/ms	$T_{1\rho}$/ms	k/s^{-1}
356		3.9	2.6×10^7
350		2.2	1.5×10^7
342		2.2	1.5×10^7
335		0.8	4.6×10^6
327		0.9	5.3×10^6
320		0.7	4.2×10^6
313		0.5	1.3×10^6
306		1.3	3.3×10^5
299		1.6	2.7×10^5
292		3.9	1.1×10^5
284	16.8	3.7	1.2×10^5
277	14.2	12.6	3.3×10^4
270	9.8	21.4	2.0×10^4
263	7.0	26.0	1.6×10^4
255	5.0		
248	3.5		
241	2.4		
233	1.5		

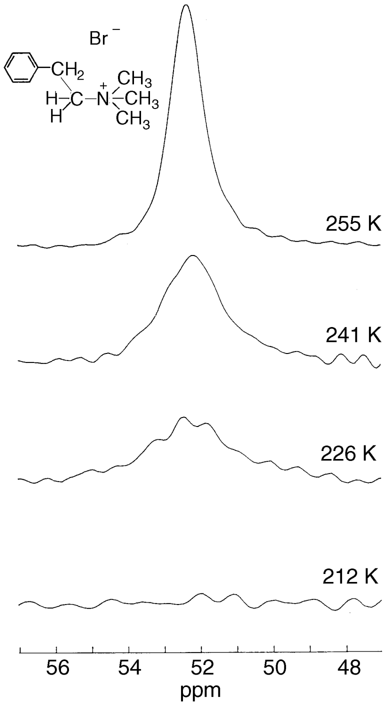

Fig. 3 Variable temperature ^{13}C CP/MAS NMR spectra of the *N*-methyl region in compound **3b** measured at 125.758 MHz

The spectrum of compound **3b** shows the *N*-methyls at 53 ppm, the benzylic CH_2 at 32 ppm, the *N*-CH_2 at 66 ppm and the aromatic carbons *ca.* 130 ppm. On cooling the intensity of the *N*-methyl signal decreases with temperature due to $T_{1\rho}$ relaxation until the signal disappears at 212 K; Fig. 3. The $T_{1\rho}$ data are shown in Table 2. The observed process is presumed to be a $-N^+Me_3$ rotation. Since the minimum value of $T_{1\rho}$ could not be measured, the experimental value of B^2 required to obtain rate constants could not be derived. (B^2 is a measure of the dipolar $^{13}C-^1H$ interaction; see ref. 5.) However, a plot of ln($T_{1\rho}$) against 1/T was made[7] which gives an activation energy, E_a, of 26.4 ± 0.9 kJ mol^{-1} for trimethylammonium rotation.

At low temperatures the aromatic carbons appear as four peaks at 123, 127, 128 and 133 ppm of which the central pair are of double intensity; Fig. 4. On heating, the central two peaks coalesce (259 K), broaden (292 K), go through a $T_{1\rho}$

Table 3 $T_{1\rho}$ and rate data for compound **3c**; ($\omega_1 = 60$ kHz)

	50 ppm	53 ppm	58 ppm	130 ppm	
T/K	$T_{1\rho}$/ms	$T_{1\rho}$/ms	$T_{1\rho}$/ms	$T_{1\rho}$/ms	k/s^{-1}
342				8.4	6.3×10^6
335				6.7	4.9×10^6
328				4.5	3.0×10^6
313				2.3	1.1×10^6
306				3.5	6.4×10^5
299				6.7	2.7×10^5
292				7.7	2.3×10^5
283				13.7	1.3×10^5
277	17.6	32.3	27.0	23.3	7.4×10^4
269	13.4	26.4	25.4	40.7	4.2×10^4
262	10.8	25.7	17.6		
255	7.8	19.0	12.5	79	2.2×10^4
247	5.6	16.7	11.8		
240	3.9	11.8	10.6		
232	2.9	8.1	6.0		
225	1.6	6.1	4.3		
218		3.1	2.6		
211		2.3	2.3		

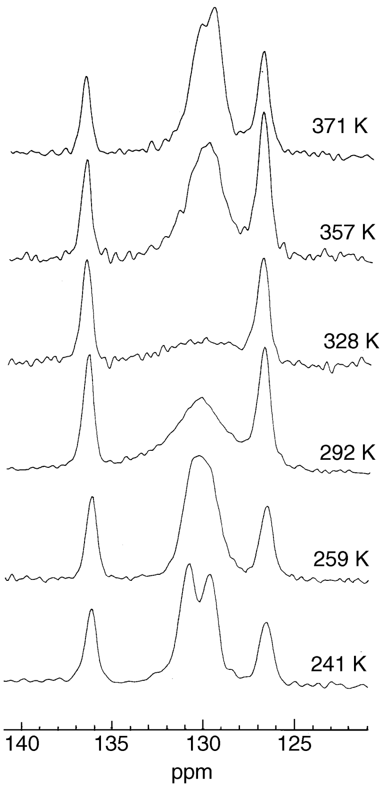

Fig. 4 Variable temperature ^{13}C CP/MAS NMR spectra of the aromatic region in compound **3b**, measured at 125.758 MHz

minimum (328 K) and sharpen (371 K). Again this is due to the rapid rotation of the phenyl ring. Only the two carbons on the axis of rotation are unaffected. The coalescence gives an approximate free energy of activation of 49 kJ mol^{-1} at 259 K. In this case it was possible to measure the $T_{1\rho}$ relaxation of the coalesced peaks (Table 2) and the results enabled the activation parameters to be determined giving $\Delta H^{\ddagger} = 63.9 \pm 6.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 75.1 \pm 20.6$ J K^{-1} mol^{-1}. Using these parameters to calculate the free energy of activation at the coalescence temperature gives $\Delta G^{\ddagger}_{259} = 44.5$ kJ mol^{-1} in satisfactory agreement with the approximate free energy of activation at coalescence. The free energy of activation at ambient temperature (293 K) is calculated to be 41.9 kJ mol^{-1}.

The ambient temperature spectrum of compound **3c** shows the CH_2 and methyl from the *N*-ethyl group at 58 and 11 ppm respectively with the *N*-methyls at 50 and 53 ppm. The benzylic CH_2 is at 66 ppm with the ring carbons at *ca.* 130 ppm. On cooling the *N*-methyls and ethyl CH_2 change in relative intensity due to $T_{1\rho}$ relaxation. The data acquired are shown in Table 3. Since no minimum for the $T_{1\rho}$ values could be measured a plot of $\ln(T_{1\rho})$ against $1/T$ was performed instead. The activation energy derived from the average slope of three very similar lines and is found to be 20.9 ± 1.7 kJ mol^{-1}. This is a remarkably low energy of activation for the rotation of an ethyldimethylammonium group (*tert*-amyl equivalent) but it is difficult to find any other probable cause for the low and temperature dependent values of $T_{1\rho}$.

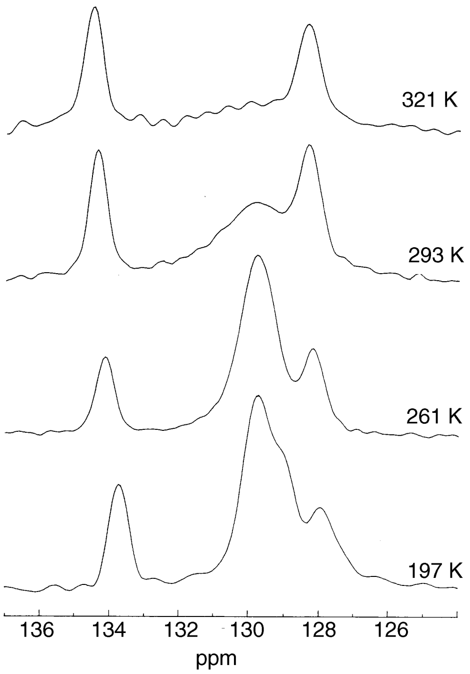

Fig. 5 Variable temperature ^{13}C CP/MAS NMR spectra of the aromatic region in compound **3c**, measured at 125.758 MHz

As with the previous two compounds, dynamic line shape changes in the aromatic region show that this sample also exhibits a phenyl group rotation; Fig. 5. At low temperatures the phenyl carbons appear as three peaks at 128, 130 and 134 ppm. The central broad peak contains the resonances of the four off-axis carbons. On heating, the relaxation becomes more rapid and the minimum intensity occurs at 313 K. The peak grows in intensity until at *ca.* 345 K, a phase change occurs and all the peaks are replaced by others. Up to this point $T_{1\rho}$ measurements were taken and the results are given in Table 3. The activation parameters for the phenyl rotation were determined to be; $\Delta H^{\ddagger} = 48.0 \pm 4.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 23.5 \pm 15.5$ J K^{-1} mol^{-1}. The free energy of activation at ambient temperature (293 K) is calculated to be 41.1 kJ mol^{-1}.

Compounds **4a**,**b**,**c** were prepared as the racemic modifications and their room temperature spectra are shown in Fig. 6.

The spectrum of compound **4a** shows the *N*-methyls at 34 and 44 ppm, and the *N*-CH at 63 ppm. The remaining methyl and benzylic CH_2 are located at 11 and 39 ppm, respectively. The aromatic carbons are at *ca.* 130 ppm. Variable temperature spectra show no significant change in the relative intensities of the peaks indicating no measurable molecular dynamics. No further data were collected on this compound.

The spectrum of compound **4b** shows the *N*-methyls and *N*-CH at 50 and 72 ppm, respectively. The remaining methyl and benzylic CH_2 appear at 13 and 38 ppm, respectively, with the aromatic carbons at *ca.* 130 ppm. At room temperature the *N*-methyls appear as one broadened peak. On cooling, the peak broadens and splits into a doublet (2:1 ratio) below 270 K; Fig.

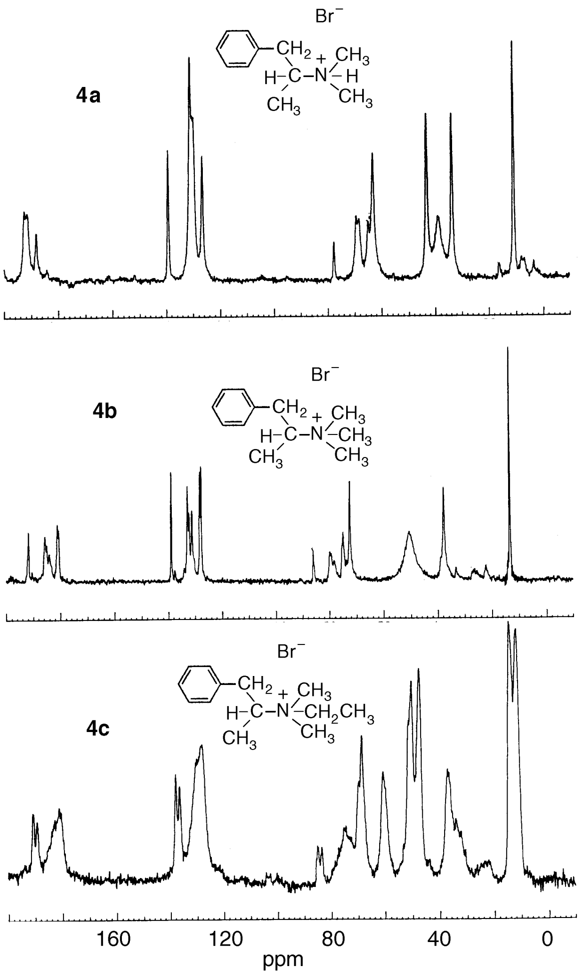

Fig. 6 Ambient temperature ^{13}C CP/MAS NMR spectra of compounds **4a**,**b** and **c** measured at 125.758 MHz

7. At higher temperatures the methyls undergo rapid $T_{1\rho}$ relaxation and the rate constants derived from relaxation measurements and line shape calculations are shown in Table 4. It was not possible to determine values above 335 K as the signal/noise ratio decreased dramatically after this point due to the cross polarisation becoming very inefficient. This could possibly have been due to a phase change. The activation parameters were determined and gave $\Delta H^{\ddagger} = 40.4 \pm 7.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = 8.0 \pm 26.7$ J K^{-1} mol^{-1}. The free energy of activation for trimethylammonium at ambient temperature (293 K) is calculated to be 42.7 kJ mol^{-1}.

The spectrum of compound **4c** shows the two *N*-methyls, *N*-CH_2 and *N*-CH at 48, 51, 61 and 69 ppm, respectively. The remaining two methyls are at 12 and 14 ppm with the benzylic CH_2 at 37 ppm. The aromatic signals are at *ca.* 130 ppm. The spectrum shows two lines for the aromatic quaternary carbon. This must be due to two molecules in the asymmetric unit (possibly enantiomeric molecules) and is probably the reason why the other peaks are broadened.† Variable temperature spectra show no significant change in the relative intensities of the peaks and we conclude that any molecular dynamics lie outwith the region we can study.

The room temperature spectra of compounds **5a**,**b** and **c** are shown in Fig. 8.

The spectrum of compound **5a** shows the two *N*-methyls and *N*-CH at 38, 43 and 68 ppm, respectively. The benzylic CH_2s are located at 32 and 38 ppm with the aromatic carbons at *ca.* 130 ppm. This compound showed no change in the relative intensities of the peaks with temperature and we conclude that any molecular dynamics lie outwith the region we can study.

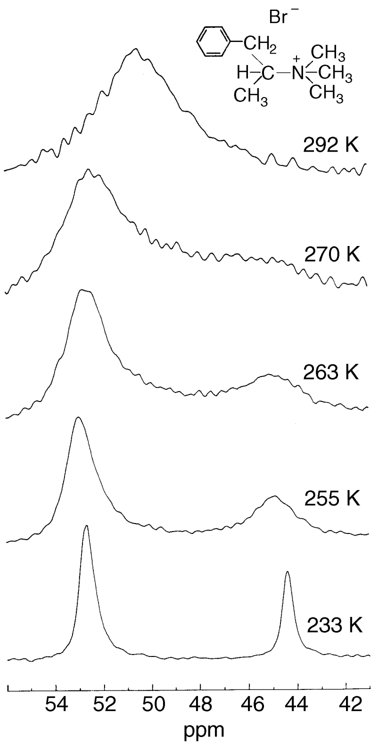

Fig. 7 Variable temperature ^{13}C CP/MAS NMR spectra of the *N*-methyl region in compound **4b** measured at 125.758 MHz

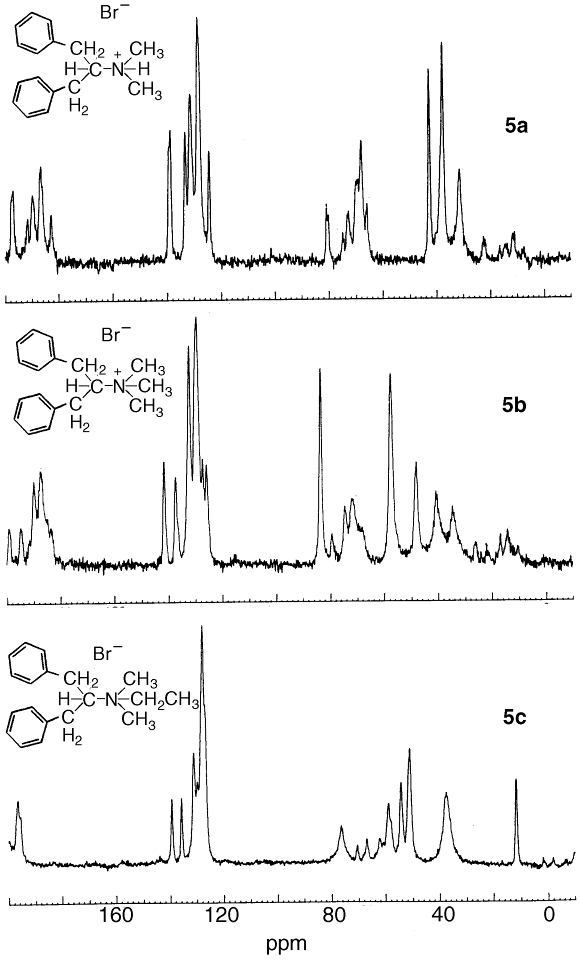

Fig. 8 Ambient temperature ^{13}C CP/MAS NMR spectra of compounds **5a**,**b** and **c** measured at 125.758 MHz

The spectrum of compound **5b** shows the *N*-methyls frozen out in a doublet (ratio 2:1) at 58 and 48 ppm. The *N*-CH is

Table 4 $T_{1\rho}$ and rate data for compound **4b**; (ω_1 = 60 kHz)

	37 ppm	50 ppm	
T/K	$T_1\rho$/ms	$T_1\rho$/ms	k/s^{-1}
335	15.9	1.5	3.2×10^6
328	15.8	1.0	1.0×10^6
320	20.9	1.6	4.5×10^5
313	25.7	1.4	3.7×10^5
306	27.7	3.0	1.9×10^5
299	46.3	4.0	1.4×10^5
292	71.6	5.4	1.0×10^5
	Line-shape data		
277			8.0×10^4
270			5.0×10^4
263			3.0×10^4
255			7.5×10^3

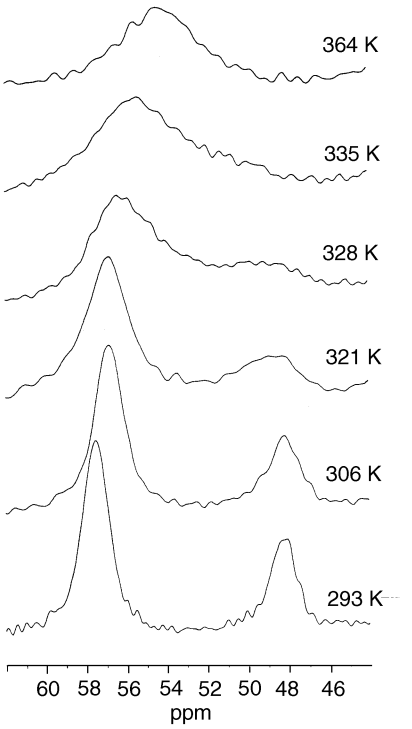

Fig. 9 Variable temperature ^{13}C CP/MAS NMR spectra of the N-methyl region in compound **4b** measured at 125.758 MHz

located at 83 ppm. The benzylic CH_2s appear at 35 and 41 ppm with the aromatic carbons at *ca.* 130 ppm. Variable temperature work done on this sample shows that on heating from room temperature to 364 K the spectra undergo dynamic line shape changes. The two methyl peaks broaden and coalesce at 328 K; Fig. 9. The approximate free energy of activation at coalescence is 51 kJ mol^{-1}. Further heating sharpens this peak. No $T_{1\rho}$ data could be gathered as the upper temperature limit of the probe had been reached.

The spectrum of compound **5c** shows the methyl from the ethyl group and two other overlapping N-methyls at 12 and 51 ppm, respectively. The N-CH_2 and N-CH are located at 54 and 76 ppm, respectively. The benzylic CH_2s are shown at 37 ppm with the aromatic carbons at *ca.* 130 ppm. Variable temperature studies showed no change in the relative intensities of the peaks and we conclude that any molecular dynamics lie outwith the region we can study.

Conclusions

These results once again illustrate the remarkable range of intramolecular mobility occurring in a simple homologous series of crystalline organic compounds. In all three compounds containing a trimethyl ammonium group the kinetics of the process and the activation energies were determined. The trimethylammonium group resembles the *tert*-butyl and trimethylphosphonium groups in the relative ease with which it can rotate in almost every solid so far examined. In each of the three compounds in series **3** a phenyl rotation was observed. This work and our earlier paper[16] show that phenyl group rotations seem to be far more common in solids than one might have imagined. Most remarkable is the very low activation energy (*ca.* 20 kJ mol^{-1}) observed for ethyldimethylammonium rotation from the relaxation data in compound **3c** but it is difficult to ascribe the data to any other process. No rotation for a dimethylammonium group was observed in this work in keeping with the failure to observe an isopropyl group rotation in our previous studies.[16]

Chemists should be aware that large segmental motions in crystalline organic compounds are the norm and not the exception.

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