Probing Molecular Motion by Solid-state NMR Spectroscopy and High Resolution Powder X-Ray Diffraction

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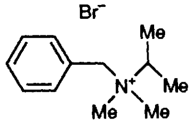
Solid-state MAS NMR spectra of benzyldimethyl(isopropyl)ammonium bromide **1** show evidence of a high activation energy for rotation of one of the *N*-methyl groups (E_a = 28 kJ mol^{-1}) whilst a powder X-ray diffraction study of **1** shows that one of the *N*-methyl groups is indeed exceptionally hindered in the solid.

Two of us (F. G. R. and M. R.) have been investigating intramolecular motions in crystalline organic compounds using ^{13}C CP MAS NMR methods and in particular have been developing the use of ^{13}C $T_{1\rho}$ measurements for studying such processes.[1–3] The ability to determine, *ab initio*, the crystal structures of organic solids from powder X-ray diffraction data is being developed by two of us (P. G. B. and P. L.). We now show that the combination of solid-state NMR and powder diffraction techniques provides a powerful means of probing molecular motions in organic crystals.

The room temperature ^{13}C CP MAS NMR spectrum of benzyldimethyl(isopropyl)ammonium bromide **1** is shown in Fig. 1. The spectrum is consistent with only one molecule in the asymmetric unit as confirmed subsequently by the X-ray diffraction. The spectrum is essentially as expected except that there is some broadening of the lines in the aromatic region. As the sample is cooled (Figs. 2 and 3) the aromatic region sharpens and the line from one of the *N*-methyl groups (δ 51 ppm), but not the other (δ 48 ppm), broadens slightly and reduces in intensity until it has vanished at 208 K. If the spectra are obtained by using single carbon pulses and high-power ^{1}H decoupling the δ 51 ppm line is visible throughout the same temperature region but broadens as the temperature is lowered. The loss of signal intensity in the CP spectra of the methyl is associated with a reduction in its ^{13}C $T_{1\rho}$ value which falls to less than 0.5 ms by 208 K.



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The reduction in the $T_{1\rho}$ value for the methyl carbon is responsible for the loss of the signal in the CP MAS spectrum as it will cause very inefficient cross polarisation. The low value of $T_{1\rho}$ is associated with the rate of rotation of the methyl group becoming comparable with the precessional frequency of the spin-locking field. A plot of $\ln(T_{1\rho})$ against $1/T$ over the region of our observations is linear and gives an activation energy of 28 kJ mol^{-1} for the rotation process.† The broadening of the line observed in the single-pulse experiment is consistent with the maximum dipolar broadening effect originally observed by Rothwell and Waugh.[6] Slowing of methyl group rotation in a crystalline organic compound has also been observed by Barrie and Anderson.[7]

As the sample is warmed a coalescence phenomenon is observed for four of the phenyl C–H carbons at temperatures around 300 K and as the sample is warmed further the coalesced aromatic carbon lines do not reemerge up to the upper limit of our measurements. We believe that the $T_{1\rho}$ effect is working again in the region above coalescence reducing the intensity of the two coalesced lines. The two carbons on the axis of rotation (δ *ca.* 128 and 129.5 ppm) are the least affected by the rotation of the phenyl group. Phenyl group rotation in solids observed by CP MAS NMR spectra has previously been reported by Twyman and Dobson[8] and by ourselves.[13]

The solid-state structure of **1** was solved by the newly emerging technique‡ of *ab initio* structure determination from X-ray powder diffraction data. We have shown that this is a viable method of obtaining structural information on organic crystals when single crystals are not available.[4,5] The packing pattern in the unit cell is shown in Fig. 4 and the molecular structure of the ammonium ion is shown in Fig. 5.

Two features of this crystal structure are particularly significant in rationalising the NMR data of the *N*-methyl group discussed above. First, the C(9) methyl group has a

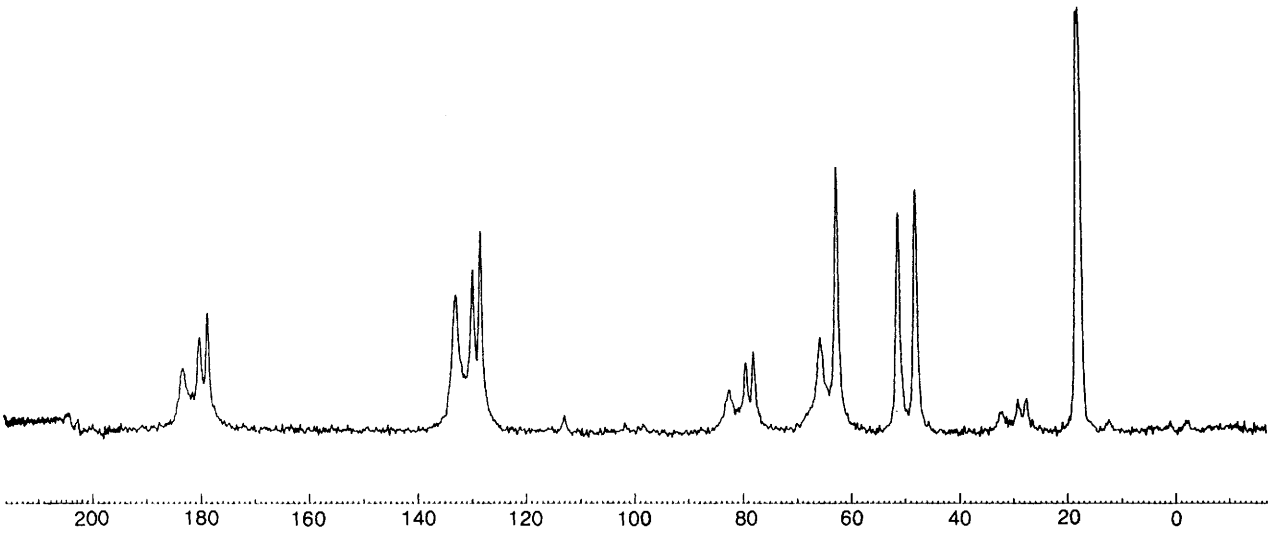

Fig. 1 Room temperature CP MAS spectrum of **1** measured at 125.758 MHz (Bruker MSL500 spectrometer). The small peaks at δ 180, 80 and 30 ppm are spinning side bands on the aromatic resonances.

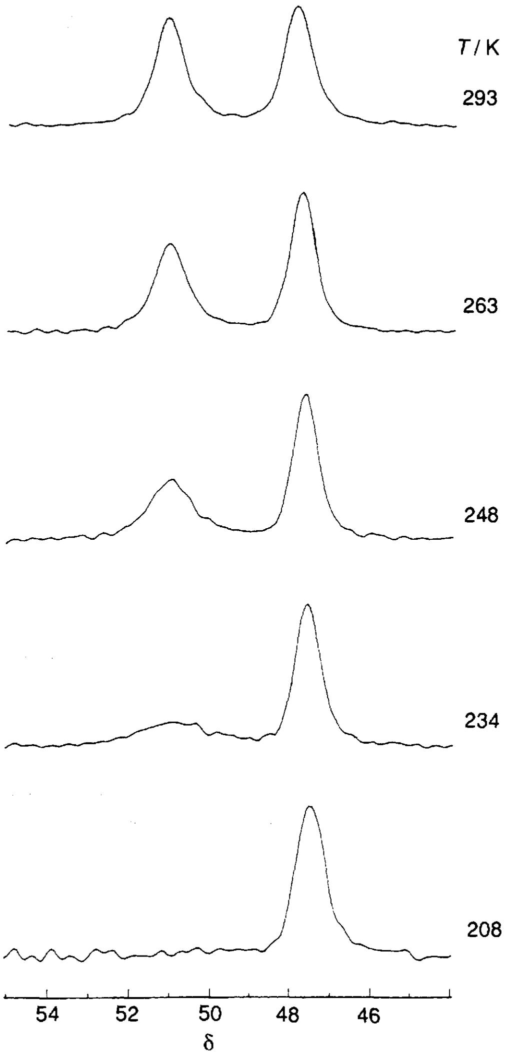

Fig 2 Temperature variation of CP MAS spectrum of the aromatic resonances

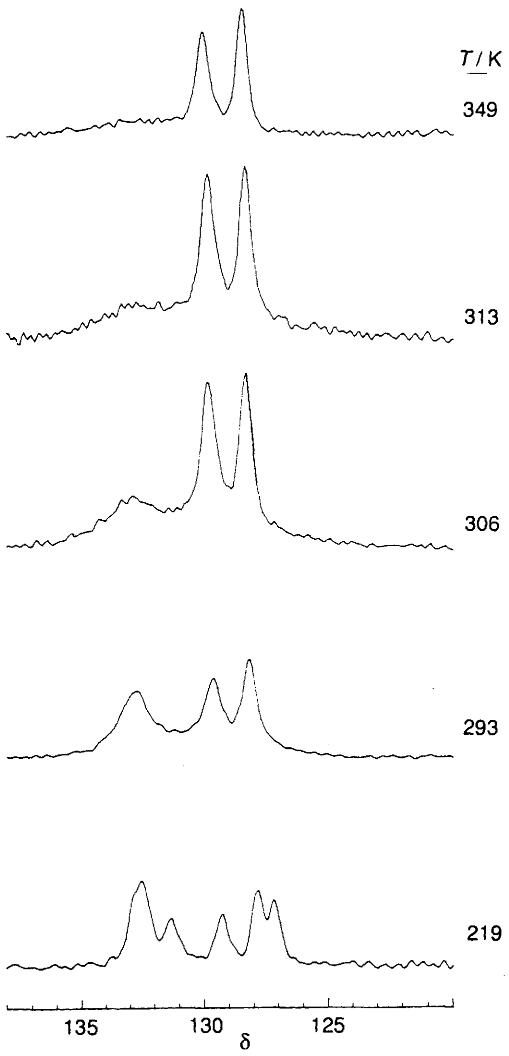

Fig. 3 Temperature variation of the CP MAS spectrum of the *N*-methyl resonances

dihedral angle of 43° along the N–C bond to one of the isopropyl methyl groups. This is significantly smaller than the ideal value of 60°. Secondly, the C(9) atom is also significantly closer to the Br^- ion than any other carbon atom, having near-neighbour Br^- ions at 368 and 385 pm. The corresponding closest contacts for the other *N*-methyl carbon, C(8), are 392 and 394 pm. The extent of the pressure exerted by the bromide upon the C(9) methyl is illustrated by the fact that the C(9) to bromide vector is in the correct direction to reduce the dihedral angle between C(9) and its isopropyl neighbour from the ideal value of 60° to the observed value of 43°. Hence the powder diffraction data clearly show that one of the methyl groups, C(9), is substantially more hindered than the other.

In addition, the crystal structure shows that the phenyl rings are relatively unencumbered. The closest approach of carbon atoms between the phenyl rings in adjacent molecules is 396 pm. One adjacent ring is parallel and the other adjacent ring is at an angle of approximately 65°. There is appreciable space in which the phenyl groups may rotate.

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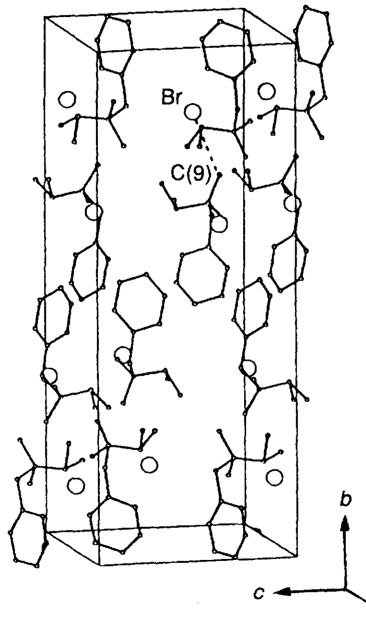

Fig. 4 The unit cell of **1** as determined from X-ray powder diffraction data. The short C(9)–Br distance is shown

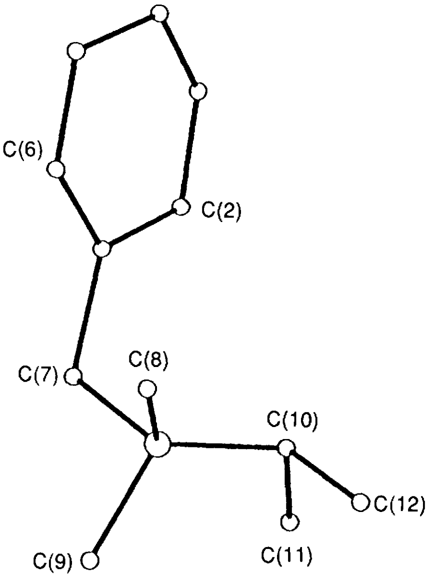

Fig. 5 The molecular structure of **1** as determined from X-ray powder diffraction data

Footnotes

† For a more detailed discussion of the use of $T_{1\rho}$ measurements to obtain activation parameters from ^{13}C CP MAS measurements see ref. 3. There follows a brief description of how E_a can be obtained from $T_{1\rho}$ measurements.

For a dipolar interaction between two unlike spins (in this case a ^{13}C in a methyl group and its directly bound ^1H), $1/T_{1\rho} = B^2\tau/(1 + \omega_1{}^2\tau^2)$, where ω_1 is the frequency of ^{13}C in the spin lock field, τ is the correlation time for the molecular motion causing the relaxation (rotational correlation time), and B^2 is a measure of the ^{13}C–^1H dipolar interaction.

We are operating in the region where $\omega_1{}^2\tau^2 \ll 1$, therefore: $1/T_{1\rho} = B^2\tau/1$ = where k $(=1/\tau)$ is the rate constant for the complete (360°) rotation of the methyl group.

$T_{1\rho}$ is thus directly proportional to k and, therefore, the Arrhenius activation plot of $\ln(T_{1\rho})$ *vs.* $1/T$ should have slope E_a.

‡ *Crystal data* for **1** $C_{12}H_{20}NBr$, $M_r = 258.2$, orthorhombic, *Pcab*, $a = 9.7610(2)$, $b = 29.896(1)$, $c = 10.0389(2)$ Å, $V = 2537.6$ Å^3, $Z = 8$, $D_c = 1.17$ g cm^{-3}. The structure was solved from X-ray powder diffraction data collected on a Stoe STADI/P transmission system, $\lambda = 1.54056$Å (Cu-Kα1). Data were collected over the range $5° < 2\theta < 85°$ in 0.02° steps, the entire run lasting about 15 hours. Data were indexed on the basis of the first 20 observable lines using the program TREOR[9] ($M_{20} = 21.6$). The pattern decomposition[10] option of the Rietveld program GSAS[11] was used to extract the first 121 integrated intensities from the powder pattern. These were used as input to the direct method program SIR,[12] from which the Br atom was located. The remaining atoms were found *via* successive difference Fourier–least-square cycles applied to Rietveld refinement of the whole diffraction profile. In the final stages of refinement, chemical constraints were added [C–C(ring) = 1.40(1) Å, C–C–C(ring) = 120°, C–C(exo) = 1.55(1) Å, C–N = 1.57(1) Å)]. Final agreement indices were $R_{wp} = 8.4\%$, $\chi^2 = 4.47$, for 59 parameters and 4018 observations (919 reflections).

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