High Resolution NMR of a Solid Organic Free Radical: ^{13}C, ^{2}H and ^{1}H Magic Angle Spinning of 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-Oxyl (TEMPOL)

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Use of highly deuteriated material has given for the first time high resolution solid state ^{13}C, ^{2}H, and ^{1}H NMR spectra of an organic free radical: 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL).

The application of high resolution solid-state NMR techniques (cross polarisation, dipolar decoupling and magic-angle spinning; CP MAS) to paramagnetic species has met with limited success to date even though ^{1}H relaxation times (T_1, $T_{1\rho}$) are not found to be impossibly short in most cases. This is to some extent surprising, since NMR observation should be favoured by the rapid electron spin exchange which should occur with

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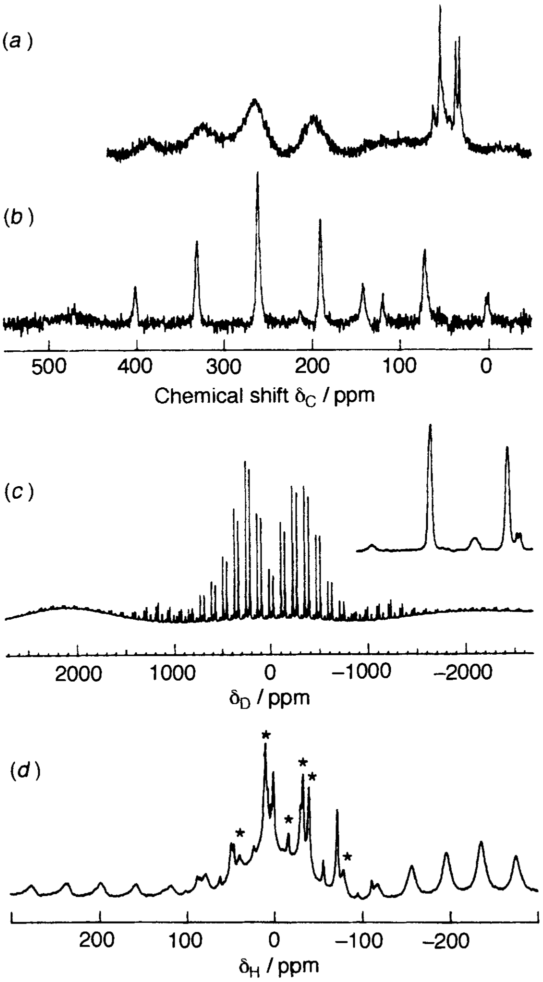

Fig. 1 Solid-state NMR spectra of TEMPOL and 97.4%-deuteriated [$^2H_{17}$]TEMPOL: (*a*) ^{13}C 75.47 MHz CPMAS of TEMPOL, ν_{rot} = 4744 Hz; (*b*) ^{13}C single pulse MAS of [$^2H_{17}$]TEMPOL, ν_{rot} = 5304 Hz; (*c*) ^2H 46.07 MHz MAS of [$^2H_{17}$]TEMPOL, ν_{rot} = 5522 Hz (inset: centreband region); (*d*) ^1H 300.13 MHz MAS of residual protons in [$^2H_{17}$]TEMPOL, ν_{rot} = 11777 Hz (centrebands denoted with asterisks). Recorded at 25 °C on a Bruker MSL-300 with 7 or 4 mm double-bearing probes and zirconia rotors. All shifts are relative to $SiMe_4$.

close packing of paramagnetic species in crystals. Published work has mostly concentrated on lanthanide complexes[1] and oxides,[2] where the electron relaxation is expected to be particularly rapid, and copper(II) complexes have also attracted attention.[3] It is known that magnetic susceptibility anisotropies can be large for paramagnetic samples, and this gives rise to a broadening which is not eliminated by MAS,[4] but this is insufficient to account for signal loss in every case.

Organic free radicals have not successfully been investigated using high resolution methods, although some ^1H work has been possible[5] at near liquid helium temperatures since the paramagnetic shifts often closely follow a $(T - \theta)^{-1}$ Curie–Weiss law and become larger than the dipolar broadening below 20 K. However, the resolution is still poor for powders and single crystal studies are not always practicable.

Recently, Clayton *et al.*[6] demonstrated that the ^{13}C MAS linewidth of europium acetate tetrahydrate was substantially improved when both the acetate ion and water of crystallisation were replaced by deuteriated forms. This was attributed to the partial failure of proton decoupling, whereas coupling between ^{13}C and ^2H and especially ^2H and ^2H is weak enough for MAS alone to give line narrowing. Here, a similar effect is reported for an organic free radical; it is also demonstrated that high resolution ^2H and ^1H spectra can be obtained.

Fig. 1(*a*) shows the ^{13}C CP MAS spectrum of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPOL),‡ a stable nitroxyl radical. The sharp peaks at δ 30–60 arise from some sample decomposition to give an unknown diamagnetic species, but one broad resonance is seen at δ 263 ($\Delta\nu_{1/2}$ *ca.* 2200 Hz) with ±1 and +2 spinning sidebands. In contrast, the deuteriated material gives a spectrum [Fig. 1(*b*)] in which two centreband lines are visible (δ 260.2 and 71.1) and which are almost an order of magnitude narrower. ^{13}C solution NMR of TEMPOL was published some time ago[7] and detection of four of the possible five resonances was reported, of which only the C-4 CHOH carbon (δ 71.2) is matched by a resonance seen in the solid.

Subsequently, it was discovered that the [$^2H_{17}$]TEMPOL sample gave a ^2H MAS spectrum [Fig. 1(*c*)] consisting of six resonances, each with an extensive sideband manifold; the isotropic shifts (δ_D/ppm) and linewidths ($\Delta\nu_{1/2}$/Hz, in parentheses) were −39.4 (70), −37.7 (70), −32.5 (110), −15.1 (210), 8.3 (110), and 39.7 (190). The high resolution is striking, and it is also notable that individual resonances have spinning sideband manifolds with very different spread; this accentuates the low centreband intensity for some peaks.

TEMPOL is known[8] to have a chair conformation in the solid state, with a mirror plane through the ring such that C(2)/C(6) and C(3)/C(5) are strictly symmetry-equivalent. The protons/deuterons within each methyl are expected to be equivalent on the NMR time scale because of fast C_3 motion, but there are inequivalent axial and equatorial hydrogens on C(3) and C(5). Thus there are six proton environments (6 : 6 : 2 : 2 : 1 : 1), but only five expected ^2H since the hydroxy proton is not isotopically substituted.

Deuterium quadrupole coupling is normally found to be axially symmetric in C–D bonds, with a quadrupole splitting of about 125 kHz. MAS should give rise to a symmetrical sideband pattern that roughly follows the static Pake doublet outline.[9] At ambient temperature the methyl groups will be rotating rapidly about the C_3 axis, averaging both the quadrupole and paramagnetic interactions. The intensities and reduced sideband ranges of the sharp peaks at δ 8.3 and −32.5 tend to indicate that these are due to the methyls. The other resonances exhibit sidebands extending to 250 kHz, indicating that the anisotropic (pseudo-contact) part of the paramagnetic coupling tensor is comparable to the quadrupole interaction. Variable temperature studies of shift and relaxation should give a full assignment, and should suggest an explanation for the small unexpected splitting on the lowest frequency resonance (δ −39.4/−37.7).

It has been shown[10] that deuterium substitution can be used to reduce the linewidth of residual protons, because the average ^1H–^1H distance is increased and the lower magnetogyric ratio reduces the dipolar couplings. The dilute ^1H spectrum is shown in Fig. 1(*d*), and spinning rate adjustment identified eight centrebands of which three sharp peaks near δ 0 seem to be due to some diamagnetic impurity or residual solvent. Exact ^1H/^2H counterpart centrebands are evident, and additionally a broad sideband family is seen extending from δ −350 to +350 with intensities indicating a *positive* paramagnetic anisotropy approaching δ 700 (210 kHz). The centreband peak is obscured by the sharper resonances, but is inferred to be at δ −78 from the change in sideband positions with spinning speed. This must be assigned to the hydroxy proton, which associates with the nitroxyl on the adjacent molecule.[8]

These results offer much clearer definition than previously for the cause of the inefficiency of ^1H decoupling in ^{13}C CP MAS of paramagnetic solids. In particular, the ^1H chemical shift range for TEMPOL at 25 °C is δ −80 to +40 *and* with large anisotropy. Practical RF field strengths are somewhat

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‡ The TEMPOL sample was obtained from Aldrich and the deuteriated sample (97.4% $^2H_{17}$) from MSD Isotopes.

less than this width (<80 kHz) so that decoupling cannot be performed *on*-resonance, and offset variation cannot overcome this. It is probable that the Curie law temperature dependence of paramagnetic shifts will give a progressive improvement as the sample temperature is raised. More importantly, decoupling performance should be better at low field strengths (B_0) and may be quite acceptable at $\nu_0(^1H)$ = 60 or 90 MHz.

Solid-state NMR spectra were obtained on the University of London Intercollegiate Research Service (ULIRS) instrument at RHBNC.

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