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Muonium addition to DMPO and PBN sorbed in silica-gel

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Nitroxyl radicals were formed by adding the light hydrogen isotope, muonium to the spin traps DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) and PBN (*N*-*tert*-butyl-α-phenylnitrone) sorbed as 30 wt% ethanol solutions in silica-gel; evidence is presented for a specific hydrogen-bonded interaction between the DMPO adduct and the silica surface; longitudinal-field muon spin relaxation measurements (LF-MuSRx) were performed which identified two distinct motional regimes in both samples.

Spin-probes, usually stable nitroxyl radicals, are widely used in the study of molecular reorientational dynamics, as detected by EPR methods.[1] In contrast, studying reactive radicals on solid surfaces poses particular difficulties for EPR detection, but these may be circumvented *via* the suite of methods available for transient radicals which have been labelled with muonium[2–5]—a hydrogen atom with a radioactive positive muon as its nucleus. It is important to connect and compare these distinct strategies.

In this aim, we have formed the radicals (**1**) and (**2**) by muonium addition to DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) and PBN (*N*-*tert*-butyl-α-phenylnitrone), both prepared as 30 wt% solutions in ethanol and sorbed in silica-gel. Although (**1**) and (**2**) are nitroxyl radicals, they are *not* stable radicals since their lifetime is limited by the radioactive decay of the muon (mean lifetime 2.2 μs). This decay permits the detection of (**1**) and (**2**), whose structures may be compared with those of chemically similar, sorbed nitroxides determined by EPR.[6] Our initial method of detection was transverse-field muon spin rotation[2,3] (TF-MuSR), the spectrum being as shown in Fig. 1 for radicals (**1**) recorded at 300 K; the lines are much broader than expected for a liquid-phase sample, indicating restricted molecular motion. A muon coupling, reduced by the muon/proton magnetogyric ratio (3.1833), of 65.6 MHz may be deduced from the sum of the TF-MuSR frequencies, in comparison with 57.4 MHz for the *all-proton* isotopomer (**3**),[7] showing an enhancement factor of 1.14 in favour of the muon–in fact a typical value for conformationally restricted radicals.[8] A similar comparison between (**2**) and (**4**) yields a reduced muon coupling of 29.1 MHz, with an enhancement factor of 1.33–this time typical of conformationally unconstrained radicals.[8]

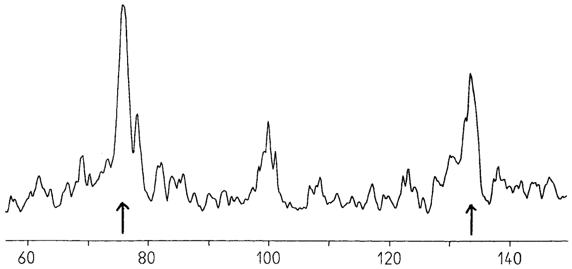
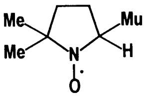
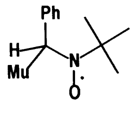


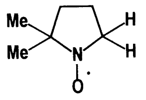
Fig. 1 Transverse-field muon spin rotation (TF-MuSR) spectrum recorded from radicals (**1**) sorbed as a 30 wt% ethanol solution in silica-gel at 300 K.



(1)



(2)



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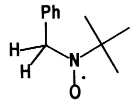
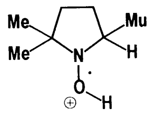


(4)



(5)

In order to probe further structural details of (**1**) and (**2**), avoided level crossing (ALC) measurements were made.[4,5] An ALC spectrum recorded from radicals (**1**) at 308 K is shown in Fig. 2, displaying *four* resonances, labelled (a)–(d). From each ALC resonance position (B_{res}), possible hyperfine couplings were calculated for ^{14}N and ^{1}H according to eqn. (1), in which A_μ and A_k are the couplings to the muon and to the other respective nucleus, and γ_μ, γ_k, γ_e are the respective gyromagnetic ratios of the muon, nucleus and electron; M is the total of their spin quantum numbers.

$$B_{res} = (A_\mu - A_k)/2(\gamma_\mu - \gamma_k) - (A_\mu^2 - 2MA_k^2)/2\gamma_e(A_\mu - A_k) \quad (1)$$

In the case of anisotropic motion, an additional resonance at $A_\mu/2\gamma_\mu$ may be expected,[4,5] arising from the pure muon 'spin-flip' transition ($\Delta m = 1$). We assign resonance (a) to the ^{14}N nucleus, for which a coupling of +52.4 MHz is derived. Corresponding to 18.7 G, the coupling is significantly greater than normally encountered for dialkyl nitroxyl radicals, which for both (**3**) and (**4**) is 15.6 G as measured in ethanol solution.[7] Resonance (b) yields either a proton coupling of +64.6 MHz using eqn. (1), or a reduced muon coupling of 65.5 MHz ($A_\mu = 2\gamma_\mu B_{res}/3.1833$) assuming it is from the $\Delta m = 1$ transition. In the latter case, the muon coupling agrees exactly with that determined from a TF-MuSR measurement made at this temperature. Indeed, accord is met over the entire temperature range 285–346 K between the coupling determined by TF-MuSR and that obtained assuming that the resonance is the pure muon spin-flip transition. Hence we assign it thus, rather than to a proton coupling. The mere observation of this resonance tells that radicals (**1**) are executing anisotropic reorientational motion. This suggests an interaction between the radicals and the surface of the silica pore which contains them.

Resonances (c) and (d) afford proton couplings of −11.5 and −26.3 MHz. ENDOR studies have been reported on related dialkyl nitroxyl radicals which show that the coupling to the

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methyl protons is of negative sign.[9] It is therefore tempting to ascribe the −11.5 MHz coupling to the six methyl protons in (**1**), although the value is much greater than is indicated by ENDOR ($\leqslant$1.6 MHz). The large ^{14}N coupling requires explanation. We note that, at 18.7 G, it far exceeds typical values for dialkyl nitroxyl radicals in protic media,[7] and approaches those measured for fully protonated nitroxyls reported by Malatesta and Ingold.[10] We believe this is the crux of the matter. Interaction of (**1**) or its precursor DMPO with the acidic silica surface leads ultimately to the protonated nitroxide (**5**). H-bonding between (**5**) and the silica surface would account for the anisotropic reorientation deduced from the $\Delta m = 1$ resonance. [In contrast, (**2**) has a 'normal'[7] ^{14}N coupling equivalent to 15.9 G, and no $\Delta m = 1$ feature was detected from it.] Since the (reduced) muon/proton isotope ratio for (**5**)/(**3**) is within the normal range,[8] there is no evidence that protonation of (**1**) increases the spin-density at the nitrogen atom, otherwise the isotope ratio would appear increased: more probably, the resulting increase in the electron withdrawing power of the oxygen atom, on protonation, causes a small degree of bending at the N-radical centre, so enhancing the ^{14}N coupling. The resulting increase in σ-character of the singly-occupied-molecular-orbital then facilitates the transmission of spin-density through the molecular σ-orbital framework, causing an increase in the methyl proton couplings from *ca* −1.6 MHz to that of −11.5 MHz measured here. It is significant that the proton couplings from the *tert*-butyl groups in di-*tert*-butylnitroxide are increased from +0.077 G[11] to *ca.* (+)0.5 G[10] on protonation in concentrated sulfuric acid. A similar enhancement from −1.6 MHz would give a coupling of *ca* −10 MHz, in accord with observation. The coupling of −26.3 MHz is ascribed to the O–H proton in (**5**). We had expected to observe additionally a resonance from the unique β-proton in (**1**)/(**5**). If the only possible contender (*i.e.* resonance (b)) had in fact been due to this, an unprecedentedly small hyperfine isotope ratio of 1.01 would pertain; given the normal isotope effect of 1.14, noted above for constrained conformations, a resonance close to *ca.* 8000 G is actually expected, but as may be judged from the field-scale shown for resonance (b), there is nothing readily convincing.

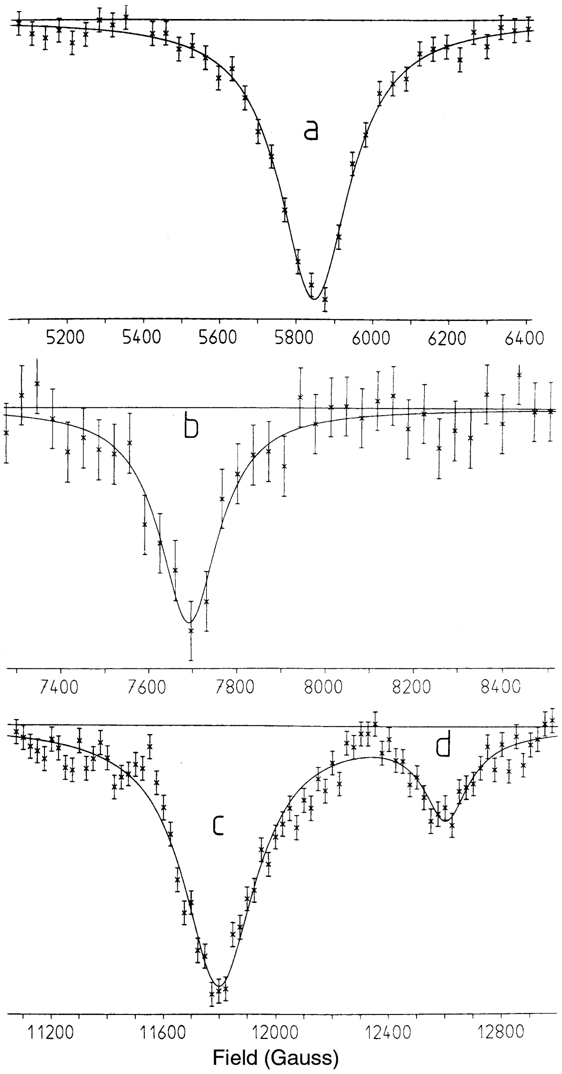

Fig. 2 Avoided level crossing (ALC) spectrum recorded at 308 K from (**1**) sorbed as a 30 wt% ethanol solution in silica-gel, showing 4 resonances (a)–(d) (see text), with relative intensities: 24, 8, 16, 5.

Longitudinal-field muon spin relaxation (LF-MuSRx) measurements[12–15] were next employed. As described in previous papers reporting on studies of sorbed radicals,[12–15] rotational correlation times were estimated from the relaxation rates measured for these radicals over the temperature range 80–300 K. Two separate motional regimes were disclosed for both (**1**) and (**2**). The appropriate Arrhenius-type plots yielded activation energies of 20.2 ± 2.0 and 11.9 ± 1.5 kJ mol^{-1} for the two kinds of motion identified for (**1**), but 16.6 ± 1.7 and 4.2 ± 0.3 kJ mol^{-1} for (**2**). We propose these arise from radicals sorbed at two distinct sites in the silica pores in each case. Some comparisons may be drawn between these results and those reported previously for nitroxyl radicals in ethanol solutions[6] and as sorbed on silica surfaces,[16–18] according to EPR measurements. The activation energies are indeed all very similar to those now determined by us, lending confidence in the parity of these widely differing experimental procedures, while that described here is applicable to the study of transient radicals in heterogeneous media, which are troublesome for EPR.[16]

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