Investigation of Naturally Abundant ^{17}O Hyperfine Satellites in the Electron Spin Resonance Spectrum of 5- and 6-Membered Cyclic Nitroxide (Aminoxyl) Radicals

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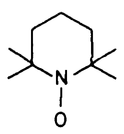
Hyperfine satellites of naturally abundant ^{17}O-isotopes have been detected for twelve nitroxide spin labels; line width, saturation, and magnetic parameters are discussed in terms of hyperfine anisotropy and molecular geometry.

Observation of ^{17}O-satellites in e.s.r. spectra can offer both structural and dynamic information about the nitroxide (aminoxyl) radicals, which are extensively used as spin labels or spin probe materials. On the basis of ^{14}N- and ^{17}O-hyperfine (hf) couplings the charge distribution within the >N–O· moiety can be determined,[1—5] and from the amplitude variation of ^{17}O-satellites valuable information can be obtained on molecular motion.[6] The ^{17}O-satellites have only been detected for non-isotopically enriched di-t-butyl nitroxide[7] and for a few ^{17}O-labelled stable nitroxide radicals. The present paper demonstrates that the ^{17}O-satellites of the e.s.r. spectra can be detected for different spin-labelled materials without isotope-enrichment and using a conventional spectrometer.

The major experimental difficulty stems from the great intensity difference between the ^{17}O-satellites and the main lines. The natural abundance is 3.7×10^{-4} and the nuclear spin is 5/2 for the ^{17}O-isotope, thus the intensity of satellites is



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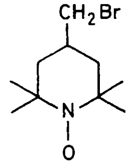

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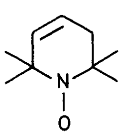

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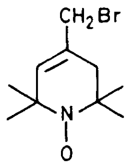

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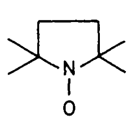

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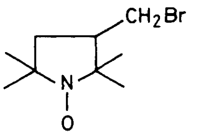

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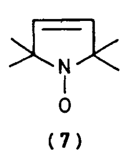

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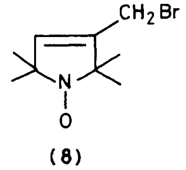

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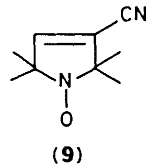

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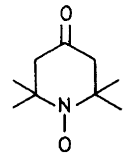

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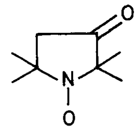

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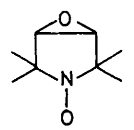

(12)

smaller by a factor of 16 000 than that of the main lines. Moreover the hyperfine coupling of oxygen is more anisotropic that that of the nitrogen,[1,2] which leads to more intensive relaxation and broader line widths for the satellites in the liquid phase. Consequently, the amplitude ratio between the main lines and the satellites is around $10^5:1$. As the tails of the big lines can suppress the small satellites any relaxation process causing line broadening should be avoided, *i.e.* the concentration of radicals cannot be too large and only deaerated solutions can be studied. The contradicting conditions of sensitivity and resolution can be compromised by using a radical concentration of around 1 mmol dm^{-3}. In order to achieve high sensitivity, toluene solutions have been studied in which the dielectric loss of microwave power is small. In a quartz tube with 4 mm inner diameter the volume sensitive to resonance is 0.4 cm^3, in which the number of radicals is 2.4×10^{17}. In the spectra of nitroxide radicals the signal intensity is shared between three nitrogen lines and, as we have seen above, the amplitude of ^{17}O-satellites is typically 10^5 times smaller, thus the equivalent spin number for the satellites is *ca.* 10^{12} radicals, which is an order of magnitude larger than the sensitivity limit of commercial e.s.r. spectrometers.

The cyclic nitroxides **(1)**—**(12)**[8—13] have been synthesized. The e.s.r. spectra were recorded on a JEOL-JES-FE/3X spectrometer with 100 kc/s field modulation. The modulation width was 0.2 mT for the satellites and 0.02 mT for the main lines; the amplification was increased by a factor of 10^3, when the satellites were recorded, thus the sensitivity difference was $10^4:1$. The magnetic field was measured using a Systron–Donner digital n.m.r. Gaussmeter with precision of 2 μT. The microwave power was 5 mW, except for the saturation experiment, where it was varied between 1 and 100 mW. The samples were deaerated by five freeze-and-thaw cycles.

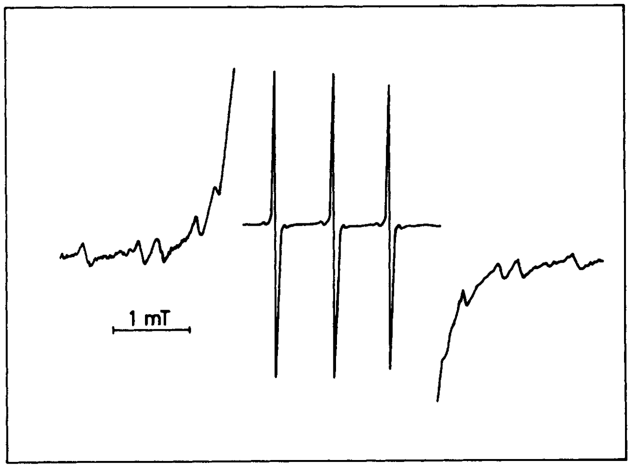

Figure 1. E.s.r. spectrum of compound **(10)** in toluene at 8 °C, the wings are recorded at 10^4 times greater sensitivity.

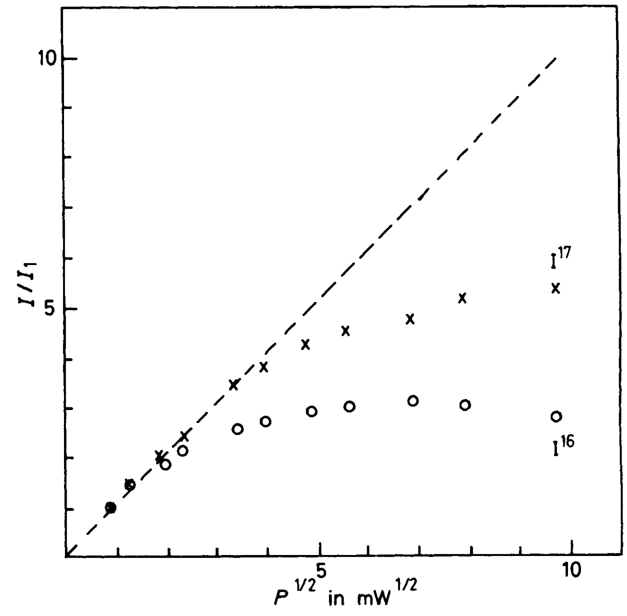

Figure 2. Amplitude variation of the first satellite (I^{17}) and first main line (I^{16}) for compound **(11)** as a function of the square root of microwave power.

The ^{17}O-satellites have been studied as a function of concentration, temperature, and microwave power. At the concentration of 1 mmol dm^{-3} the five outermost satellites on both ends of the spectra can be detected (Figure 1). At higher concentrations the main lines are broadened and the satellites are suppressed around a concentration of 10 mmol dm^{-3}. The broadening depends on the temperature, too. At lower temperature, where the exchange interaction between paramagnetic centres is weaker, somewhat larger concentrations can be used. Below −30 °C the relaxation due to magnetic anisotropy can broaden the lines and prevents detection of ^{17}O-satellites.

In the fast rotation limit, where the amplitudes of the main triplet are nearly identical and the line shape is strongly perturbed by the small proton couplings, the satellites can give more reliable relaxation times. Owing to the strongly anisotropic ^{17}O-hf interaction the satellites are selectively

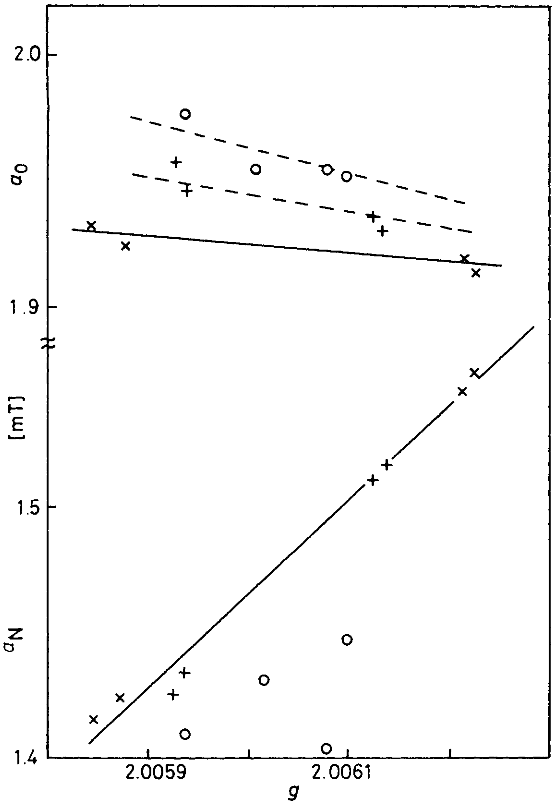

Figure 3. ^{17}O and ^{14}N hyperfine constants *vs.* *g* values at 8 °C, × for (**1**), (**2**), (**5**), (**6**); + for (**3**), (**4**), (**7**), (**8**); and ○ for (**9**)—(**12**).

Table 1. Magnetic parameters for nitroxide radicals.[a]

Compound	*g*	a_O (mT)	a_N (mT)
(**1**)	2.00623	1.915	1.555
(**2**)	2.00622	1.918	1.548
(**3**)	2.00614	1.931	1.518
(**4**)	2.00613	1.937	1.506
(**5**)	2.00588	1.924	1.423
(**6**)	2.00585	1.932	1.416
(**7**)	2.00594	1.945	1.434
(**8**)	2.00593	1.958	1.427
(**9**)	2.00594	1.976	1.409
(**10**)	2.00610	1.950	1.447
(**11**)	2.00606	1.953	1.403
(**12**)	2.00602	1.954	1.432

[a] All data are obtained in toluene solutions at 8 °C.

broadened and the inhomogeneous broadening of unresolved patterns plays a minor role. This can be demonstrated by the amplitude ratio of the first main and satellite lines. For (**1**) and (**2**) where the proton coupling constants are relatively large[14] this ratio is 4.4×10^4, while for (**10**), where the proton splittings are small,[14] it is 13×10^4 at 8 °C. At lower temperature this ratio is significantly larger, *e.g.* at −30 °C it is 50×10^4 for (**10**). For more concentrated samples and at higher temperatures the exchange interactions broaden both the satellites and the main lines and the amplitude ratio can be close to the 1.6×10^4 theoretical limit. Similar trends can be observed for the saturation behaviour of the satellites and main lines. According to Figure 2 the main lines start to be saturated above 4 mW, the satellites are saturated only above 10 mW. This means that the spin–lattice relaxation is stronger for the satellites, which can be explained by the large hf anistropy of ^{17}O.

Structural information can be obtained from Figure 3 where the ^{17}O and ^{14}N-hf coupling constants are plotted against the *g* factor for the twelve cyclic nitroxide radicals. The oxygen coupling is less sensitive to the structure of the ring, than the nitrogen coupling, though a_o is somewhat larger for the radicals with non-saturated rings. The slightly increased a_O and decreased a_N values show a charge shift towards the oxygen in the case of CN, oxo, and epoxy substitution. In the case of non-substituted and CH_2Br substituted compounds remarkably good correlation can be seen between a_N and *g*. This correlation can be related to the geometrical change of the C(C)–N–O group. This ring was planar for the five-membered rings and (**10**) and pyramidally distorted for the piperidine ring as shown in *X*-ray diffraction studies.[15] This is in agreement with the large a_N values for the six-membered rings (see Table 1), since the distortion-induced sp-hybridization gives an additional contribution to the s electron spin density on the nitrogen.[1,16] The relation between the geometry and the *g* values has not yet been analysed. We assume that the red shift of the $n \rightarrow \pi^*$ transition,[17] which is caused by the pyramidal distortion through the weakening of π-bond of the NO group, is the cause of the larger *g* value in the distorted structure. This explanation is supported by the data of Grinberg,[18] who measured larger g_{xx} for the pyramidal (**1**), than for the planar (**10**), while g_{yy} and g_{zz} were found to be less sensitive to the geometry.

Received, 19th July 1985; Com. 1055

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