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Advantages of FT NMR for Measuring Long-Range ^{14}N Hyperfine Couplings and Its Application to 2,2-Diphenyl-1-picrylhydrazyl (DPPH)

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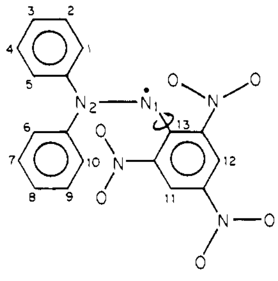
We report here, to our knowledge, the first application of high-field Fourier-transform (FT) NMR to the measurement of small ($\leq$1 G) ^{14}N hyperfine coupling (A^N) for large organic free radicals. As an example we have chosen the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) (I). DPPH was chosen because although this was one of the first radicals to be studied by EPR[1] and has later been studied extensively by ELDOR,[2] NMR,[3] electron nuclear double resonance (ENDOR),[4,5] and triple resonance (TRIPLE),[5] its EPR hyperfine (hf) structure is still not understood, largely because the hf couplings from the three NO_2 nitrogens have not been amenable to direct measurement. The most detailed study of the hf structure of DPPH is that of Biehl et al.[5] These authors have used EPR, (deuteron) NMR, ENDOR, and TRIPLE resonance techniques, but were still unable to measure NO_2 couplings directly. It is known[6] that the difficulty in measuring small ^{14}N hf couplings by EPR arises from the inhomogeneous broadening caused by the splittings due to other nuclei, while the failure of ENDOR and TRIPLE resonance techniques is thought to be due to the low γ_N of the ^{14}N nucleus, short relaxation times (T_2) and the low spin density since ENDOR enhancement goes to 0 as γ, A, and T_2 go to 0 as shown by Freed and others.[6] These conclusions had earlier provided a motivation for exploring the use of NMR to supplement the ENDOR and TRIPLE resonance studies. In particular, it was thought[7,8] that for the ^{14}N measurements, broad-line NMR, utilizing magnetic field modulation, would be ideally suited. However, the actual measurements on DPPH showed[8] that the observed spectra were poor in terms of both the signal-to-noise ratio and the spectral resolution (as may be noted from Figure 1e). In particular, the observed NMR signal line shape had indicated that the ^{14}N hf couplings from the three NO_2 groups were inequivalent and that $A^N_{ortho} > A^N_{para}$, whereas the present study demonstrates that, in fact, $A^N_{ortho} < A^N_{para}$.



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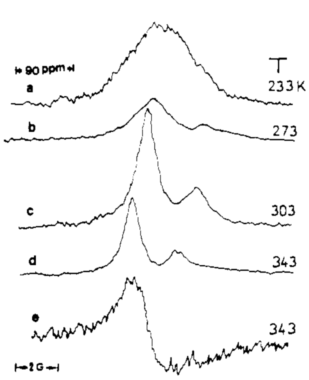

Figure 1. ^{14}N (NO_2) NMR spectra of DPPH. Spectra a–d were taken at 13.0 MHz and e was taken at 4.3 MHz as discussed in the text.

The ^{14}N NMR measurements were made at a frequency of 13.004 MHz with a Bruker SPX-180 pulse spectrometer. The sharpest signals were obtained with the CH_2Cl_2 solutions containing ~1% di-*tert*-butyl nitroxide (a spin relaxer).[7] The contact shifts were measured relative to the NO_2 resonances of diphenylpicrylhydrazine, the precursor of DPPH. Variable-temperature studies (over 230–340 K) showed that the contact shift, ΔH, obeyed (to within 4%) the inverse temperature relationship,[7] demonstrating that the shift is dominated by the isotropic hyperfine interaction.

Figure 1 shows typical ^{14}N NMR spectra of a saturated (~0.5 M) solution of DPPH in CH_2Cl_2. The spectra shown in Figure 1a–d were obtained at 13.006 MHz. The spectrum in Figure 1e was obtained at 4.334 MHz and $T = 340$ K, as in ref 8. The comparison of 1d with 1e clearly exhibits a significant enhancement in both the signal-to-noise ratio and the resolution in the FT measurements.

The observation of two well-resolved signals in Figure 1a–d shows that in the investigated range (230–343 K), the A^N (NO_2) couplings fall into two sets. A comparison of the relative signal intensities suggests that the smaller A^N corresponds to two magnetically equivalent nitrogens and the larger A^N to only one. This observation by itself is insufficient to assign the coupling to specific NO_2 groups since molecular packing models of DPPH show[4,5] that it contains no symmetry elements. However, the temperature dependence of the NMR line shapes and earlier proton ENDOR studies of DPPH[4,5] provide a clue to the signal assignment. The ENDOR studies[5] showed evidence for hindered rotation of the picryl ring about the $C_{13}N_1$ bond. Similar results were obtained from proton NMR of the DPPH precursor,[9] 2,2-diphenyl-1-picrylhydrazine, the motion being fast on the NMR time scale. The presence of fast motion already at ~250 K implies that if the line of higher intensity belonged to one ortho and one para nitrogen, then a further increase in temperature would lead to a broadening and eventual coalescence of this signal with the

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Table I. ^{14}N hf Couplings for the NO_2 Groups in DPPH

technique	$A^N{}_{ortho}$, G	$A^N{}_{para}$, G	ref
computer simulation of EPR spectra	0.754	0.377	13
Fourier transform analysis of EPR	0.38	0.33	14
combined EPR and proton ENDOR	1 ± 0.3	0.7 ± 0.3	4
theoretical values using Hartree-Fock spin densities plus			
(a) Karplus-Fraenkel approach	−1.56	−1.14	4, 5, 10, 11
(b) Nanda et al. approach	−0.27	−0.25	4, 5, 10, 12
CW NMR at 4.3 MHz and computer simulation	−0.46 ± 0.02	−0.38 ± 0.02	8
	−0.39 ± 0.02	−0.48 ± 0.02	8
FT NMR at 13.0 MHz	−0.38 ± 0.02	−0.48 ± 0.03	this work

other peak. If, however, the higher intensity NMR signal corresponds to the two ortho nitrogens, then an increase in temperature above 250 K would lead to either further narrowing or no change in the spectra. Figure 1a–d shows the latter to be the case, thereby establishing that $A^N{}_{ortho} = -0.38 \pm 0.02$ G and $A^N{}_{para} = -0.48 \pm 0.03$ G.

However, the assignment of $A^N{}_{para} > A^N{}_{ortho}$ is in conflict with the current theoretical models for estimating ^{14}N hf couplings,[10-12] since all these calculations predict[8] that $A^N{}_{para} < A^N{}_{ortho}$. The reliability of the reported spin densities was suggested by a very good agreement between the calculated[10-12] and the observed values[4,5] for the proton hf couplings in DPPH. The disagreement for the ^{14}N results suggests that the ^{14}N couplings can provide a very sensitive probe of the accuracy of the wave functions for large free radicals. Table I shows a comparison of the results from various techniques.

The temperature dependence of the observed line widths of the o-NO_2 signal was studied over 230–343 K. The line width decreased sharply with the increase in temperature, indicating motional narrowing. The line-width variation could be analyzed by employing the modified Bloch equations.[15] In the regime of "fast" motion, the line broadening, $\delta\omega$, caused by motional effects is given by[15]

$$\ln (\delta\omega) = \ln [(\Delta W)^2/(8P_0)] + E_a/(kT)$$

E_a being the activation energy and the other symbols having usual meanings. Thus if motional effects are the dominant cause of line broadening, then the plot of $\ln (\delta\omega)$ vs. $1/T$ should be linear, with slope E_a/k. This was indeed found to be the case, thus supporting the hindered rotational model. A least-squares fitting of the plot yielded $E_a = 6.3 \pm 1$ kcal/mol. This value is in agreement with that (~7 kcal/mol) determined by Heidberg et al.[9] for the picryl ring motion in the parent hydrazine (when account is taken of the stabilization due to the hydrogen bonding) and 5 ± 0.2 kcal/mol for DPPH as determined[5] via proton ENDOR.

The present work establishes the following: (a) FT NMR can be used to measure small (≤ 1 G) ^{14}N hf couplings. (b) The unexpectedly large ^{14}N NMR line widths observed earlier[8] were due to the hindered motion of the picryl ring, with an activation energy of 6.3 ± 1 kcal/mol. (c) Whereas fast relaxation reduces the effectiveness of the EPR/ENDOR/TRIPLE resonance techniques, it helps FT NMR. (d) The available models[10-12] of spin distribution and hf splittings in large organic radicals do not accurately predict nitrogen couplings, and the present results can form a basis for further improvement. We envisage applications of this technique to large biological systems where long-range ^{14}N hf couplings are often expected.

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Registry No. 2,2-Diphenyl-1-picrylhydrazyl, 1898-66-4.

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Isomeric σ and π Radicals from Carboxylic Acids and Amides

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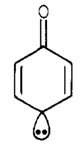
The possibility of orbital isomerism[2] in conjugated systems where one conjugated atom has a lone pair of electrons seems to have first been pointed out by Dewar and Narayansawami[3] in the case of the carbene **1**. Excitation of a lone-pair electron into an empty π MO normally gives rise to $n \rightarrow \pi^*$ excited state (cf. A → B in Figure 1) but if the π LUMO is a bonding or nonbonding MO of low energy and if the "excited state" (cf. **2**) differs from the "ground state" in geometry, the two states may correspond to different local minima on the potential surface separated by an energy barrier (cf. A → C → D in Figure 1). Note that **1** and **2** are distinct isomers because their wave functions differ in symmetry, that of **1** being symmetric and that of **2** antisymmetric, for reflection in the π nodal plane.



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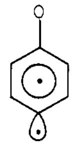

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Analogous orbital isomerism is clearly possible in conjugated radicals where the unpaired electron can occupy either of two MOs of comparable energy, one σ and one π, the two MOs containing one or three electrons between them. Radicals of this type derived from amides, imides, or carboxylic acids by loss of a hydrogen atom, e.g., **3–5**, play an important role in various reactions, and their structures have been the subject of much recent work.[4-9]

$RCO\dot{N}H$	$(RCO)_2N\cdot$	$RCOO\cdot$
3a, R = H	**4a**, R = H	**5a**, R = H
b, R = CH_3	b, R = CH_3	b, R = Ph
c, R = CF_3	c, R = CF_3	c, R = CH_3
		d, R = CF_3

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(1) Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina.

(2) Orbital isomers are defined as species distinguishable by different occupation of a set of available MOs. The MOs may be distinguished by symmetry, as here, or by their nodal properties. See: Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5242.

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