tion of 1.5 Hz between the central lines. Assuming a typical geminal coupling constant of *ca.* 12 Hz, this means $\delta_{AB} \sim 6$ Hz for the benzylic protons in the solvents studied.

2-Phenylethanol-2,2-d_2 was prepared as described[21] and converted into the (*R*)-O-methylmandelate ester. Deuterium-decoupled spectra in pyridine and carbon tetrachloride showed only a singlet for the $-CH_2O$ protons, with half-width of *ca.* 0.6 Hz; the line width in benzene was 1.0 Hz. Assuming natural line widths of 0.4 Hz (appropriate to our spectrometer) the observed line width of 0.6 Hz implies that the central lines of the AB pattern are separated by less than 0.2 Hz. With $J_{AB} = 12$ Hz this means $\delta_{AB} \leqslant 2.2$ Hz. Spectra of the alcohol itself in (+)-α-naphthylamine also showed a sharp singlet of line width 0.7 Hz.

Acknowledgment. This work was supported by National Science Foundation Grant GP-7939. Acknowledgment is made to the donors of the Petroleum Research Fund for partial support of this research.

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Electron Spin Resonance Studies of Nitronylnitroxide Radicals with Asymmetric Centers[1]

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Abstract: We have investigated the esr spectra of two nitronylnitroxide radicals with substituents containing asymmetric centers. The asymmetric center is bonded to a methylene group adjacent to the heterocyclic ring. The methylene protons are magnetically nonequivalent and exhibit different hyperfine coupling constants. Some of the peaks in the esr spectra are observed to broaden with decreasing temperature. The temperature dependence of the spectra is explained by a model involving hindered interconversion of conformers.

Investigations of π-electron organic radicals with aliphatic substituents have produced information about the mechanism of coupling to the aliphatic protons.[3] Couplings to the first group of protons on the aliphatic chain have been shown to depend on the twist angle between the 2p orbital on the unsaturated carbon and the plane defined by the two carbon atoms and the hydrogen. The empirical relation which has been used to relate the coupling constant (a_i), the twist angle (θ), and the spin density at the unsaturated carbon (ρ_2) is given by

$$a_i = [B_0 + B\cos^2\theta]\rho_2 \qquad (1)$$

B_0 and B are constants with values estimated to be +3 and +45 G.

Rotation about the carbon–carbon single bond is normally rapid at room temperature and the observed spectrum is a time average of the various conformations available for a given molecule. If one considers a methylene group bonded to the unsaturated carbon, one will observe the normal three-line spectrum from coupling to two equivalent hydrogens. The magnitude of the coupling constant will depend on the values of the angles in the various conformations which are averaged by rotation. If rotation is slow one may observe the spectrum from a given conformation in which the twist angles for the two protons and their respective coupling constants are different. At intermediate rates of rotation, the inner lines in this four-line spectrum may be broadened.[4] This line broadening results from partial time averaging of the energy levels responsible for these transitions.

We have investigated the nmr and esr spectra of the nitronylnitroxide radicals shown in Figure 1. The asymmetric center bonded to the α-carbon atom makes the two α-hydrogens geometrically nonequivalent. These two hydrogens may therefore have different average twist angles in the various conformations. Rotation about the C_2–C_α bond will not interchange the two sets of twist angles and the protons will be nonequivalent. In the limit of rapid conformational interconversion, the coupling to the two nuclei will result from a time average of the different sets of twist angles.

We have examined the esr spectra of these radicals in toluene and in aqueous solutions of different pH. In most cases different couplings were observed from the two α-methylene hydrogens. Variable temperature studies conducted with toluene as the solvent showed a broadening of some of the lines with decreasing temperature.

Experimental Section

The nmr spectra were taken on a JEOLCO 4H-100 nmr spectrometer equipped with a 35-Hz broad line unit. Esr spectra were taken on a JEOLCO 3BSX esr spectrometer.

2-(2′-Phenylpropyl)-1,3-dioxy-4,4,5,5-tetramethyldihydroimidazole (1). 3-Phenylbutyraldehyde[5] (1.0 g, 6.75 mmole) and 2,3-bis(hydroxylamino)-2,3-dimethylbutane[6] (1.0 g, 6.75 mmole) in

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[1] Synvar Research Institute Contribution No. 8: Studies of Stable Free Radicals. V.

[2] (a) University of Rochester; (b) Synvar Postdoctoral Fellow, 1968–1969; (c) Synvar Research Institute.

[3] F. Yamauchi and R. W. Kreilick, *J. Amer. Chem. Soc.*, **91**, 3429 (1969); E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); C. Heller and H. M. McConnell, *ibid.*, **32**, 1535 (1960).

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Table I. Nmr Shifts and Coupling Constants[a]

Compd	Solvent	a^N	$\alpha(1)$		$\alpha(2)$		β		γ-CH$_3$		Ring CH$_3$	
			Shift	a	Shift	a	Shift	a	Shift	a	Shift	a
1	CDCl$_3$, DBNO		21.7	−2.93	10.4	−1.41	1.35	+0.18	0.28	−0.038	1.58	−0.21
1	Toluene (esr)	7.25		2.96		1.22						0.22
1	H$_2$O, pH 7 (esr)	8.10		3.0		0.91						
1	H$_2$O, pH 2 (esr)	8.10		3.0		1.05						
2	CDCl$_3$, DBNO		16.75	−2.26	14.15	−1.91	1.27	+0.17	0.25	−0.034	1.50	−0.20
2	Toluene (esr)	7.36		2.32		1.92						0.22
2	H$_2$O, pH 7 (esr)	8.0		2.75		1.28						
2	H$_2$O, pH2 (esr)	7.9		1.9		1.9						

[a] The shifts are in kilohertz from the corresponding peak in a diamagnetic molecule. The coupling constants are in gauss.

25 ml of benzene were stirred for 1 hr at 30°. After addition of 10 g of lead dioxide and stirring for an additional 10 min, the mixture was filtered through Celite, dried over magnesium sulfate, and evaporated *in vacuo*. Chromatography of the residue with 4:1 ether–benzene on silica yielded the deep red crystalline radical **1**, mp 120–122°, *m/e* 275 (M).

Anal. Calcd for $C_{16}H_{23}N_2O_2$: C, 69.78; H, 8.41; N, 10.17. Found: C, 69.91; H, 8.46; N, 10.16.

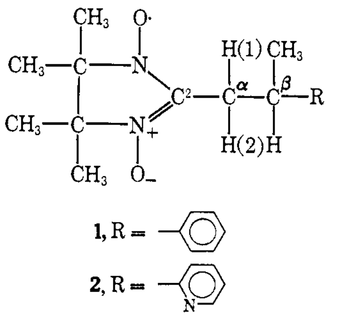

Figure 1. Compounds investigated.

2-[2′-(α-Pyridyl)propyl]-1,3-dioxy-4,4,5,5-tetramethyldihydroimidazole (2). A solution of 2-ethylpyridine (13.9 g, 130 mmole) in 50 ml of ether was added dropwise under nitrogen to 60 ml of 2 *M* phenyllithium in benzene. After boiling this mixture for 30 min, chloroacetaldehyde diethyl acetal (9.91 g, 65 mmole) was added and the mixture was then heated for 5 hr followed by stirring at room temperature for an additional 12 hr. Addition of water and extraction with ether yielded after distillation 7.0 g (49%) of a pale yellow oil, bp 83–85° (0.05 mm). Redistillation gave pure 3-(α-pyridyl)butyraldehyde diethyl acetal: bp 98–99° (0.3 mm); *m/e* 223 (M); nmr (100 MHz, CCl$_4$) τ 1.53 (1 ArH, d of d, J_{AB} = 6 Hz, J_{AC} = 2 Hz), 2.53 (1 ArH, t of d, J_{CD} = 8 Hz, J_{AC} = 2 Hz), 3.01 (2 ArH, M), 5.80 (1 OCHO, d of d, J_{AX} = 5 Hz, J_{BX} = 7 Hz), 6.60 (2 CH$_2$, M), 7.05 (CH, M), 7.80–8.39 (CH$_2$, M), 8.76 (CH$_3$, d, J = 7 Hz), 8.89 (CH$_3$, t, J = 7 Hz, 8.92 (CH$_3$, t, J = 7 Hz).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.49; N, 6.27. Found: C, 69.95; H, 9.28; N, 6.27.

This acetal (2.0 g, 8.96 mmole) was hydrolyzed by boiling in 29 ml of 0.03 *N* hydrochloric acid for 15 min followed by neutralization of the reaction mixture and extraction with ether. The oil obtained from the ether extracts was stirred for 2 hr at room temperature with 1.33 g (8.96 mmole) of 2,3-bis(hydroxylamino)-2,3-dimethylbutane in 50 ml of ether. The oil obtained by removal of the solvent was stirred in 50 ml of benzene with 13.3 g of lead dioxide for 10 min at room temperature. Filtration through Celite, evaporation of the filtrate *in vacuo*, and chromatography with 1:9:10 methanol–ethyl acetate–benzene on silica yielded a deep red solid. Recrystallization from ether–petroleum ether (bp 30–60°) gave 0.97 g (39%) of the radical **2**, mp 113–116°, *m/e* 276 (M).

Anal. Calcd for $C_{15}H_{22}N_3O_2$: C, 65.19; H, 7.96; N, 15.21. Found: C, 65.36; H, 7.71; N, 15.33.

Results and Discussion

The radicals were very soluble in chloroform-*d* and we were able to observe nmr peaks from all of the protons except those of the α-methylene group in this solvent. The lines from the α-methylene protons could be observed when the radicals were dissolved in either di-*t*-butylnitroxide (DBNO) or in mixtures of DBNO and chloroform-*d*.[7] The positions of the other lines in the spectra were not affected by this change in solvents.

The hyperfine coupling constants (a_i) are related to the shifts of the lines (ΔH) by

$$a_i = -\frac{\Delta H}{(\gamma_e/\gamma_N)\left(\dfrac{g\beta H}{4kT}\right)} \tag{2}$$

Shifts and coupling constants for the various protons are given in Table I. The line from the methyl groups bonded to the heterocyclic ring and from the γ-methyl group were shifted to high field indicating negative coupling constants at these positions. The peak from the single β proton was shifted to low field. The lines from the protons in the aromatic rings were not shifted from their normal positions. Two signals shifted to high fields were observed from the α-methylene protons. The values of the coupling constants obtained from the nmr spectra were almost identical with those determined from the esr spectra of the radicals in toluene.

Esr spectra of the radicals in toluene were taken at a series of different temperatures. The two α-methylene protons were nonequivalent and five groups of quartets were observed at room temperature. Splittings from the ring methyl protons were resolved and each of the peaks in the quartets appeared as a group of lines. The difference in the coupling of the two α-methylene protons of radical **2** was small and the lines in the inner groups of quartets were somewhat overlapped. As the temperature was lowered, the intensity of the inner lines decreased until they were lost in the base line. The width of the peaks in the outer groups remained constant over the temperature range investigated. When higher modulation levels were used the splittings

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(7) R. W. Kreilick, *J. Amer. Chem. Soc.*, **90**, 5991 (1968); *Mol. Phys.*, **14**, 495 (1968).

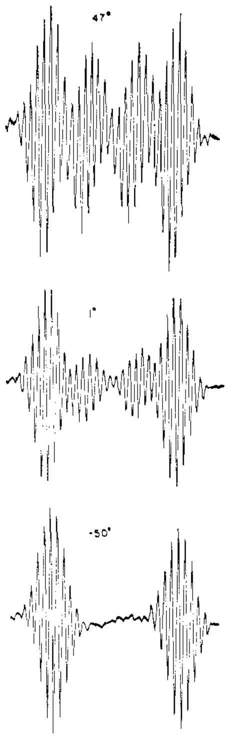

Figure 2. High-resolution esr spectra of the center group of lines from radical **1** at various temperatures.

from the methyl protons were not resolved. Spectra taken under these conditions did not show the loss in intensity of the inner lines until the samples were cooled to much lower temperatures. Representative spectra of compound **1** are shown in Figures 2 and 3.

The changes in relative intensities can be explained by a broadening of the inner peaks with decreasing temperature. The relation between the line widths and intensities is given by

$$W_i = \left[\frac{I_0 W_0^2}{I_i}\right]^{1/2} \tag{3}$$

where W_i = width of inner peaks, I_i = intensity of inner peaks, W_0 = width of outer peaks, I_0 = intensity of outer peaks. Equation 3 was used directly to calculate line width from relative intensities in the case of radical **1**. The two inner lines in the spectrum of compound **2** were overlapped and it was necessary to multiply the ratio of intensities by a correction factor. The center lines in the inner groups were overlapped with the third line from the adjacent inner group. If the line widths had been equal, the center lines in the inner groups should have been a factor of 1.5 more intense than the corresponding lines in the outer groups. Line broadenings were obtained by substracting the natural line width from the total width determined by eq 3. A plot of the log of the line broadening *vs.* the reciprocal of temperature is shown in Figure 4.

The spectra observed at higher temperatures appear to result from a rapid time averaging of various molecular conformations. The broadening of the inner peaks of the quartets at lower temperatures results from a slower rate of interconversion of the various conformations. The absence of broadening of the outer lines indicates that the energy levels for these transitions are nearly the same in all of the conformations. The time average of the sum of the α-methylene coupling constants must be the same in each of the conformations in order for these levels to have constant values.

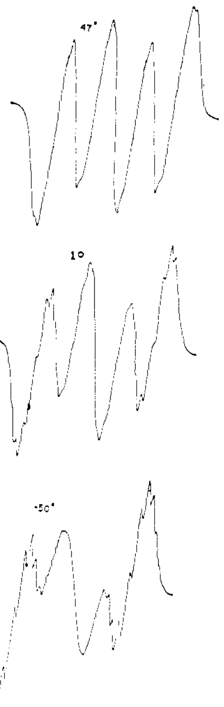

Figure 3. Low-resolution esr spectra of the center group of lines from radical **1** at various temperatures.

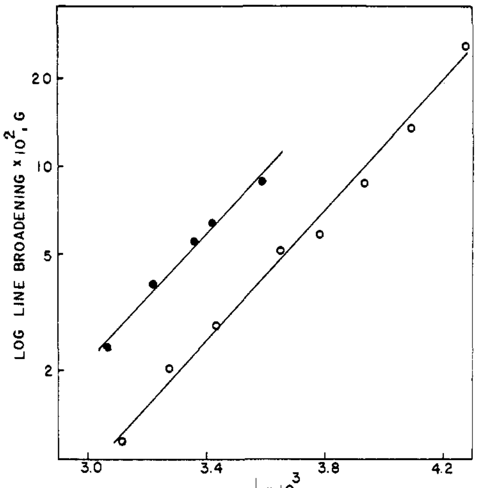

Figure 4. Plot of the log of the line broadening *vs.* the reciprocal of temperature: ○, phenyl; ●, pyridyl.

In order to calculate the rate of conformational interconversion, one must know the coupling constants and populations of the individual conformations which are being averaged. We were unable to observe the spectra from the individual conformations and we therefore were unable to determine the rates of interconversion accurately. The line widths should vary linearly with the lifetimes of the individual states. If this is the case, one can determine the activation energies for interconversion from the slopes of the lines in Figure 4. The activation energies obtained by this technique are 4.3 kcal for radical 1 and 4.2 kcal for radical 2.

Esr spectra of the radicals were taken in aqueous solution at various pH's. The spectrum of radical 1 was almost independent of pH. The coupling constants were slightly different from those observed in toluene (Table I). The spectrum of radical 2 showed a marked pH dependence. In basic or neutral solutions the α-methylene protons were not equivalent and five quartets were observed. The methyl splittings were not resolved. As the pH was lowered the inner lines moved together, broadened, and collapsed into a single line. The intensity of this line was not twice that of the outer lines indicating that the protons are not completely equivalent at low pH values. The pH dependence of the spectrum probably results from protonation of the pyridine nitrogen at lower pH. If the average twist angles in the protonated species are different from those of the free base one predicts a change in the coupling constants. Differences in solvation may also affect the twist angles and be partially responsible for the changes in the methylene couplings with solvent and pH.

A full account of the pH dependence of the spectra of **2** and other nitronylnitroxides will be presented elsewhere.

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Nuclear Magnetic Resonance Spectra of *endo*-Bicyclo[2.1.0]pentan-2-ol, Cyclobutanol, and *cis*-1,3-Dibromocyclobutane[1]

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Abstract: Detailed analyses of the nmr spectra of the title compounds have been performed. The results permit one to compare the coupling constants for planar and puckered cyclobutane rings. The planar ring gave J_{cis} = 9 and J_{trans} = 3.5 Hz. The puckered ring gave J_{ae} = 9.7 and 7.9, J_{aa} = 10.4, and J_{ee} = 2.3 Hz. All of these values are in agreement with those expected based on the dihedral angles. The long-range coupling between equatorial hydrogens was 5.2 and 5.6 Hz and had a positive sign. The coupling constants for two related cyclobutane derivatives were found to be quite similar suggesting that the values given herein should provide useful starting points for the analysis of other cyclobutanes.

Although considerable data are now available on the nmr spectra of cyclopropane derivatives,[2] relatively few simple cyclobutanes have been studied.[3] One reason is that the nmr spectra of cyclobutane derivatives are generally quite complex and involve large numbers of overlapping lines. This makes the analysis of the spectra quite difficult.

It was of particular interest to us to examine representative compounds in which the difference in coupling constants between a planar cyclobutane ring and a puckered ring could be obtained. Thus, we have studied the bicyclo[2.1.0]pentan-2-ols[4] in which the cyclobutane ring will be forced into near planarity by fusion to a cyclopropane ring and cyclobutanol in which the ring would be expected to be puckered by 30–35°.[5] As an added check on the cyclobutanol parameters, the spectrum of *cis*-1,3-dibromocyclobutane[6] also was studied.

The 100-MHz spectra of the two isomeric bicyclo[2.1.0]pentan-2-ols are shown in Figures 1a–e and Figures 2a–c, respectively. The one later identified as the *exo* isomer consisted of four multiplets and a hydroxyl band. The two high-field multiplets represent one hydrogen each and almost certainly correspond to the cyclopropyl methylene hydrogens. The low-field multiplet must correspond to the hydrogen adjacent to the hydroxyl group. The remaining four hydrogens lead to a single complex multiplet.

The spectrum of the *endo* isomer is much simpler since each multiplet corresponds to only one hydrogen. Again the two high-field multiplets must result from the cyclopropane methylene hydrogens, and the low-field multiplet corresponds to the hydrogen adjacent to the hydroxyl group. In the following discussion, the seven multiplets and the corresponding hydrogen atoms have been numbered from 1 through 7 in the direction of increasing field.

Initial decoupling experiments at a 500-Hz sweep width provided identification of all large coupling constants in the spectrum of the *endo* isomer even though fine details could not be observed. Multiplets 3, 4, and 7 were complex patterns which resembled quartets of

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[1] This investigation was supported by the U. S. Army Research Office. The nmr spectrometer was obtained through a departmental instrument grant from the National Science Foundation.

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[4] K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Am. Chem. Soc.*, **90**, 5338 (1968).

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