Nuclear Magnetic Resonance Studies of Phenoxy Radicals. Coupling to Protons on Aliphatic Chains

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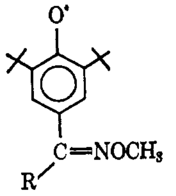
Abstract: We have taken the nmr and esr spectra of a series of phenoxy radicals with aliphatic substituents. The liquid radical di-*t*-butyl nitroxide was used as a solvent for the nmr experiments. Rapid spin exchange between solvent and solute radicals averaged the electron spin states and allowed us to observe relatively sharp nmr lines. Couplings to the aliphatic protons were observed in each case. The couplings to these protons are discussed in terms of three types of interaction.

In an earlier paper we described magnetic resonance measurements which were conducted on a series of phenoxy radicals with cyclic aliphatic substituents.[1] These experiments were carried out to obtain information about the coupling of the odd electron to protons in the cyclic aliphatic substituent. We have extended this work to a series of phenoxy radicals substituted with aliphatic chains. The nmr spectra of these radicals were used to determine proton coupling constants. Nitrogen couplings were determined from esr spectra. The compounds which have been investigated are



1, R = CH_3
2, R = CH_2CH_3
3, R = $CH_2CH_2CH_3$
4, R = $CH_2CH(CH_3)_2$
5, R = $CH(CH_3)_2$
6, R = $C(CH_3)_3$

The liquid radical di-*t*-butyl nitroxide (DBNO) was used as a solvent for the nmr experiments. Rapid spin exchange between solute and solvent radicals averaged the electron spin states and allowed us to observe relatively sharp nmr lines.[2] The shifts of the nmr lines (ΔH) are related to the electron–nuclei coupling constants (a_i) by

$$a_i = -\frac{\Delta H}{\left(\frac{\gamma_e}{\gamma_N}\right)\left(\frac{g\beta H}{4kT}\right)} \qquad (1)$$

Lines from protons with smaller coupling constants could be observed in chloroform-*d* in some instances.

The phenoxy radicals can exist as two different geometric isomers. Representations of the *syn* and *anti* structures are given in Figure 1. A single set of lines were observed from compounds **1–4**. These compounds are thought to be in the *anti* conformation. Compound **5** exhibited lines from both isomers while compound **6** appeared to be entirely in the *syn* conformation.

The coupling of the odd electron to protons on the aliphatic chains was of particular interest. In our earlier paper, these splittings were discussed in terms of two types of interactions. Coupling to protons on β-carbon atoms have been explained by a hyperconjugative mechanism.[3] The angular dependence of these splittings has been interpreted by the empirical relation given in eq 2,[4,5] where B_2 is a constant with a

$$a_B = Q(\theta)\rho_\alpha \qquad Q(\theta) = B_0 + B_2\cos^2\theta_2 \qquad (2)$$

value between 40 and 50 G, ρ_α is the spin density at the α-carbon atom, and B_0 relates the coupling constant to the spin density at the α-carbon atom when θ_2 is 90°. For freely rotating methyl groups $\langle Q(\theta)\rangle$ is taken to have a value between 20 and 25 G.

When θ_2 is 90° the coupling of the β protons may be accounted for by a spin polarization mechanism. Longer range couplings in the series of radicals which were previously studied could also be explained by spin polarization.[1] When this type of interaction is responsible for the splitting, the coupling constants are related to the spin density at the α carbon by[5]

$$a_i = Q_i\rho_\alpha \qquad (3)$$

A different polarization constant should be found for each group of nuclei on the aliphatic chain. A third mechanism which can contribute to the splittings of protons on aliphatic chains involves a direct overlap of the alkyl hydrogens 1s orbital with a pπ orbital containing unpaired spin.[6] In favorable conformations certain groups on the aliphatic chains might be positioned near enough to the π system for this type of interaction to be important.

Experimental Section

I. Compounds. A. Radicals. The radicals were made by oxidation of the corresponding phenols with aqueous alkaline $K_3Fe(CN)_6$ by the technique previously described.[1] Short oxidation times (*ca.* 5 min) were found to give the best yields. The samples contained diamagnetic impurities which were used as internal references. Samples for esr experiments were made by oxidation with PbO_2. Carbon tetrachloride was used as a solvent for the esr experiments.

B. Phenols. The phenolic oximes were made from the corresponding ketones by methods previously described.[7,8] The

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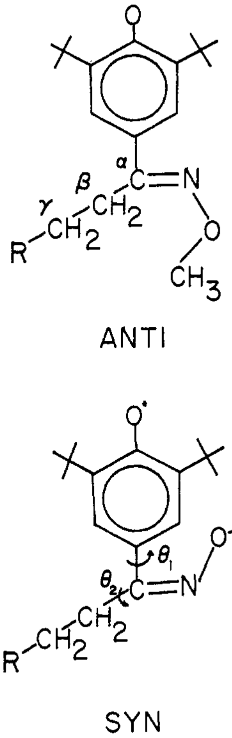
Table I. Analytical Data, Melting Points, and Yields of the Ketones and Oximes[a]

	Theoretical		Found			
	% C	% H	% C	% H	Mp, °C	% yield[b]
		(1) Ketones				
CH_2CH_3	78.0	9.94	77.7	9.96	138	32
$CH_2CH_2CH_3$	78.2	10.1	78.1	10.3	85	25
$CH_2CH(CH_3)_2$	78.7	10.3	78.9	10.5	111	12
$CH(CH_3)_2$	78.2	10.1	78.1	10.3	140	25
		(2) Oximes				
CH_2CH_3	74.3	10.0	74.2	10.1	47	53
$CH_2CH_2CH_3$	74.7	10.2	74.7	10.3	55	56
$CH_2CH(CH_3)_2$	75.2	10.3	75.4	10.2	66	49
$CH(CH_3)_2$	74.7	10.2	74.5	10.0	95	62

[a] The preparation of compounds **1** and **6** are described in ref 7. [b] Yields of ketones are after four recrystallizations from CCl_4; yields of oximes are after two recrystallizations from aqueous methanol.

ketones were made by the method of Matsuura.[9] Analytical data, melting points, and yields for the new compounds are given in Table I. The chemical shifts of the diamagnetic oximes are given in Table II.



ANTI

SYN

Figure 1. Geometry of *syn* and *anti* isomers and labeling of the positions.

II. Instruments. The nmr spectra were taken on a JEOLCO 4H-100 nmr spectrometer with a 35-Hz broad-line attachment. Calibrations were made with an audiooscillator. The esr spectra were taken on a JEOLCO 3BSX esr spectrometer with 100-kHz field modulation. Spectral simulations were carried out with a JEOLCO RA-1 digital computer.

Results and Discussion

The nmr spectra of the radicals exhibited peaks from the aromatic, *t*-butyl, methoxy, and aliphatic protons. Representative spectra are shown in Figures 2 and 3. The values of the shifts and coupling constants are given in Table III. The lines from the aromatic and *t*-butyl protons were shifted to low field. The coupling to these protons was almost constant for this series of compounds. The line from the methoxy protons was shifted to low field and retained a relatively constant value for compounds **1**–**5**. These radicals are thought to exist in the *anti* conformation. A second methoxy peak from the *syn* isomer was observed in the spectra of radical **5**.

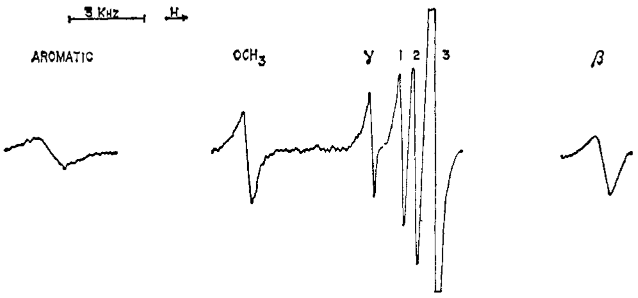


Figure 2. Nmr spectrum of radical **4** in DBNO. Various regions of the spectrum are recorded at different gains. Lines 1, 2, and 3 refer to the radical's *t*-butyl line, the diamagnetic *t*-butyl line, and the DBNO line, respectively.

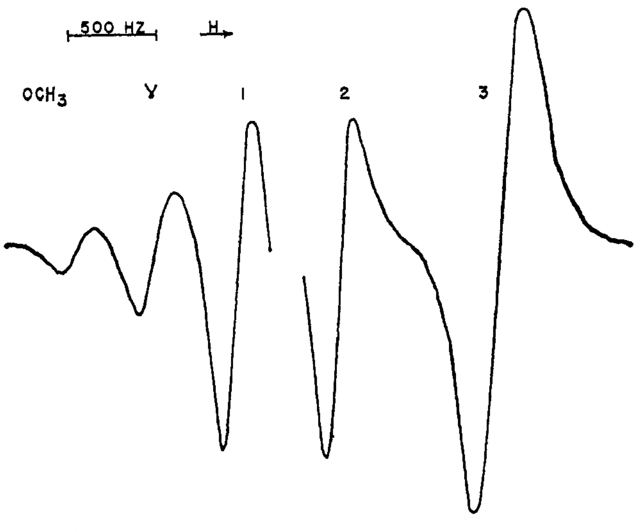


Figure 3. Nmr spectrum of radical **6** in DBNO. The aromatic line is not shown. See caption to Figure 2 for explanation of lines 1–3.

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Table II. Chemical Shifts of the Oximes[a]

R	*t*-Butyl	OCH_3	OH	Aromatic	β[b]	γ[b]	ϵ[b]
CH_3	1.45	3.90	5.13	7.37	2.12		
CH_2CH_3	1.45	3.93	5.27	7.45	2.70	1.13	
$CH_2CH_2CH_3$	1.46	3.95	5.20	7.42	2.68	~1.46	1.0
$CH_2CH(CH_3)_2$	1.46	3.89	5.12	7.39	2.57	~1.46	0.92
$CH(CH_3)_2$	1.42	3.90, 3.79[c]	5.21	7.20, 7.11[c]	3.47	1.17	
$C(CH_3)_3$	1.44	3.64	5.05	6.68	...	1.11	

[a] Units are parts per million in $CDCl_3$. [b] Center of group of lines. [c] *syn* isomer

Table III. Shifts[a] and Coupling Constants of the Radicals

R	N[b]	*t*-Butyl		Aromatic		OCH_3		β		γ	
	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G
CH_3	3.7	0.54	+0.072	13.7	+1.82	6.26	+0.83	12.77	−1.70		
CH_2CH_3	3.7	0.49	+0.065	13.8	+1.84	6.10	+0.81	7.13	−0.95		
$CH_2CH_2CH_3$	3.7	0.49	+0.065	13.6	+1.81	6.08	+0.81	7.07	−0.94	0.97	+0.128
$CH_2CH(CH_3)_2$	3.7	0.49	+0.065	14.0	+1.86	6.40	+0.85	7.45	−1.02	1.64	+0.218
$CH(CH_3)_2$	3.7	0.52	+0.069	13.5	+1.80	4.96	+0.66	2.23	−0.30		
						2.15[c]	+0.29				
$C(CH_3)_3$	0.84	0.55	+0.073	14.0	+1.86	1.18	+0.16			1.0	+0.134

[a] The shifts are from the corresponding peak in the diamagnetic phenols. [b] The estimated error in the nitrogen coupling constant is ±0.1 G. [c] Peak from *syn* isomer.

Radical **6** and its phenolic precursor appear to be in the *syn* conformation. The aromatic and methoxy lines of the phenol are shifted upfield with respect to the corresponding lines from the other compounds. These shifts indicate that this molecule is in a twisted conformation with the methoxy group positioned above the aromatic ring.[10] The methoxy splitting from the radical is smaller than that observed from the other compounds because of the lower spin density at the nitrogen in the twisted conformation.

The electron spin resonance spectra of the radicals exhibited splittings from most of the nuclei. Couplings from the *o*-*t*-butyl protons were resolved in each case, and the spectra were very complicated. Spectral simulations were carried out to obtain the value of the nitrogen coupling constant. The proton coupling constants obtained from the nmr experiments were used. Good fits were obtained for all of the spectra except the spectrum from compound **5**. In this case we had to decrease the methoxy coupling by 0.08 G and increase the β-proton splitting by 0.07 G to obtain a good simulation. The nitrogen coupling constant was almost constant for compounds **1**–**5**. The nitrogen splitting from radical **6** was much smaller, indicating a large change in the value of θ_1.

The variation in the couplings of the β hydrogens can be explained by eq 2. If rotation around the bond between the α- and β-carbon atoms is hindered and the compounds have different equilibrium conformations, one predicts the observed variation in the coupling constants.[5] The nitrogen splittings of radicals **1**–**5** are almost identical, indicating that the spin densities at the α carbons are similar. The spin density at the α carbon has been determined for the radical in which a hydrogen was bonded to the α-carbon atom[1] ($\rho_\alpha = -0.103$ with $Q_{C-H} = -22.5$ G; $\rho_\alpha = -0.082$ with $Q_{C-H} = -27$ G). The nitrogen splitting of this radical is close to that observed from compounds **1**–**5**. If the methyl carbon of radical **1** is freely rotating, one can estimate $\langle Q(\theta) \rangle$ from the values of the methyl protons coupling constant and ρ_α. Our values for $\langle Q(\theta) \rangle$ are +16.8 and +21 G for respective spin densities at the α carbon.

The values of the coupling constants from the three compounds with two β protons are nearly identical. The similarity in these splittings indicates that the barrier to rotation is not very dependent on the nature of the alkyl group bonded to the carbon. The splitting from the single β proton in compound **5** was the smallest observed, and it was almost identical with the coupling observed from a number of the compounds with cyclic substituents. If these compounds exist in a conformation in which θ_2 is 90°, one can calculate a value of about +3.0 G for B_0.

The value of the γ coupling constants varied over a large range. We were unable to observe a line from these protons in the spectra of compounds **2** and **5** and have assumed that this peak is overlapped with the line from the *o*-*t*-butyl protons. The line from the γ protons of the radical with a cyclopropyl substituent was not observed in our previous study. The nine γ protons of compound **6** have a relatively large coupling although the spin density at the α carbon should be considerably lower in this radical.

If spin polarization is solely responsible for the γ couplings, they should be proportional to the spin density at the α-carbon atom (eq 3). The variation in these splittings suggest that another mechanism is contributing to the couplings. A direct polarization of the γ hydrogens 1s electron by spin at the *para* position of the phenoxy ring can account for these observations. The spin density at this position is predicted to be large and positive. A direct interaction with the hydrogens would result in a positive contribution to the coupling constant.

Spin polarization should also produce a positive coupling at this position, and one may observe the sum of these two interactions. In the case of compounds **2** and **5** the conformation for a direct interaction would be unfavorable, and the splittings would result solely from spin polarization. We estimate that the minimum observable value for the γ coupling constant would be

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0.09 G. Values for the spin polarization parameter with this coupling constant are $Q_\gamma = -0.87$ G with $\rho_\alpha = -0.103$; $Q_\gamma = -1.1$ G with $\rho_\alpha = -0.082$. The coupling of the γ hydrogens in radicals **3** and **4** is larger because of a contribution from a direct interaction with spin on the phenoxy ring. Compound **6** appears to be in a twisted conformation in which the γ protons are in close proximity to the aromatic ring. The nitrogen splitting from this radical is about a factor of 4.5 smaller than that observed from the other radicals, indicating a decrease in the spin density at the α carbon. The splitting from the γ protons of this compound is probably dominated by a direct interaction with spin at the *para* position of the phenoxy ring.

Lines from the ϵ protons of compounds **3** and **4** were not observed. Small negative couplings were observed from this position in the cyclic compounds. Contributions from spin polarization and from a direct interaction would have opposite signs for these protons. If the interactions are of a comparable magnitude, they would tend to cancel one another. In the case of the cyclic compounds, the geometry of the rings prohibits a direct interaction and these splittings are observable.

Conclusions

The nmr and esr spectra of a series of alkyl-substituted phenoxy radicals have been taken. Different interactions appear to be important in determining the coupling constants of the various aliphatic protons. The splitting constants of β protons seem to be dominated by a hyperconjugative mechanism. Both spin polarization and direct interaction appear to contribute to the longer range couplings.

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Electron Delocalization in Paramagnetic Metallocenes. II. Extended Huckel Molecular Orbital Calculations[1a,b]

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Contribution from the W. A. Noyes Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois. *Received October 16, 1968*

Abstract: Self-consistent charge extended Hückel molecular orbital calculations were carried out for vanadocene, methylvanadocene, cobaltocene, methylcobaltocene, nickelocene, and methylnickelocene. For these calculations, Basch, Gray, Viste VOIP's were used for the H_{ii}'s and the Wolfsberg-Helmholz approximation was used for the H_{ij}'s. The overlap matrices were computed using Clementi's SCF atomic functions. The molecular orbital calculation gives a generally good account of the experimental facts for the metallocenes, in particular the nmr contact shifts. It was found that the primary unpaired electron delocalization mechanism for vanadocene and chromocene involves σ MO's. This is in agreement with our earlier experimental conclusions. In cobaltocene and nickelocene, unpaired electron delocalization is dominated by the π contribution, but the σ effects are quite large. In all cases the magnitudes and signs of the coupling constants are well reproduced.

In the first paper of this series[3] the experimental results pertaining to the nmr contact shifts of the paramagnetic metallocenes were presented. It was suggested that the unpaired spin delocalization mainly involves cyclopentadiene σ orbitals in the vanadium and chromium metallocenes (by σ orbitals we mean the in-plane orbitals of the cyclopentadiene rings, it being recognized that there is no strict σ separation in this case). It was further argued that π delocalization probably is most important for cobalt and nickel metallocenes. In order to further clarify the experimental facts, we have carried out extended Hückel molecular orbital calculations for these metallocenes. The extended Hückel method was chosen because of the possibility of including all the valence orbitals of both the metal and the ligands.

Self-consistent field type molecular orbital calculations have been reported for various metallocenes by Shustorovich and Dyatkina[4-6] and Dahl and Ballhausen.[7] Unfortunately, all these calculations included only the cyclopentadienyl p_z orbitals and are therefore unsuitable for discussions of electron-proton hyperfine interaction constants.

The extended Hückel method has enjoyed considerable success in the treatment of various transition metal complexes. Cotton and coworkers have carried out extended Hückel calculations for $PtCl_4^{2-}$,[8] $ReCl_6^{2-}$, $OsCl_6^{2-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$,[9] $Re_2Cl_8^{2-}$,[10] and bis(β-ketoenolate) complexes of Cu(II) and Ni(II).[11] It is

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(1) (a) Abstracted from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; (b) presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Paper M-42.

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