$C_3H_4^+$, $C_3H_3^+$, and $C_3H_2^+$ Ions. Little can be said about the structure of these ions, and they are listed only in the hope that future determinations will find the energetic data useful. As with the $C_4H_2^+$ ion, the almost total uncertainty as to the origin of these ions makes a calculation of a heat of formation virtually impossible.

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Magnetic Resonance Studies of Some Phenoxy and Nitroxide Biradicals

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Abstract: We have taken the nmr and esr spectra of a series of phenoxy and nitroxide biradicals. The susceptibilities of these compounds were measured by monitoring the shifts of internal diamagnetic reference peaks as a function of radical concentration. The sign and magnitude of most of the electron-nuclei coupling constants could be determined from these data. In some instances we were able to measure singlet-triplet energy separations. Both the contact shifts and the susceptibilities were measured at a series of different temperatures.

In a series of earlier papers we have reported the nmr spectra of a number of organic monoradicals.[2] The liquid radical di-*t*-butyl nitroxide (DBNO) has been used as a solvent for a second solute radical. Rapid spin exchange between solute and solvent molecules averages the electron spin states, and one is able to observe relatively sharp nmr lines. The sign and magnitude of the electron-nuclei coupling constants can be determined from the shifts of the nmr lines.

The same general technique can be used to obtain the nuclear resonance spectra of biradicals. This type of study is of particular interest, as in many cases the dipolar interaction between the two electrons of the biradicals broadens the esr spectra and one is unable to determine coupling constants. The equation relating nmr shifts ($\Delta\nu$) to coupling constants (a_i) is given by

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{contact}} = -a_i\chi_m/Ng_N\beta_N g\beta \qquad (1)$$

If the spin energy levels are defined by singlet and triplet functions, the molar susceptibility (χ_m) is given by[3]

$$\chi_m = \frac{S(S+1)g^2\beta^2 N}{3kT}\left[\frac{1}{1+\exp(\Delta G/RT)}\right] \qquad (2)$$

ΔG is the energy separation between the singlet and triplet states and is defined: $\Delta G = G(\text{triplet}) - G(\text{singlet})$. If one introduces eq 2 into 1, one obtains an equation for the shifts in terms of ΔG and a_i.

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{contact}} = \frac{-a_i g\beta S(S+1)}{3kT[1+\exp(\Delta G/RT)]} \qquad (3)$$

If independent measurements of contact shifts and susceptibilities are made, it is possible, in some instances, to obtain the values of both a_i and ΔG.

The volume susceptibilities of the biradicals can be determined from susceptibility shifts of diamagnetic solvent peaks.[4] The relation between the volume susceptibility and the shift given by

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{susceptibility}} = \frac{2}{3}\pi\Delta\chi \qquad (4)$$

If susceptibilities are determined by this technique one can calculate ΔG from eq 2 and determine coupling constants from the contact shifts.

The biradical's coupling constants should depend on the magnitude of the exchange integral for the two spins.[5] The spin-Hamiltonian which has been used to describe the hyperfine and exchange interactions can be written as

$$H = a(S_1\cdot I_1 + S_2\cdot I_2) + JS_1\cdot S_2 \qquad (5)$$

In this expression J represents the exchange integral, and I_1, I_2, S_1, and S_2 are the nuclear and electron spin operators. In cases in which $a \gg J$, the biradical acts as two separate monoradicals with each electron interacting with n_1 nuclei on a given side of the molecule. In this case one observes $2n_1I + 1$ lines in the esr spectra with a separation of a. When J is greater than a, both electrons interact with all of the nuclei (n_2) and one observes $2n_2I + 1$ lines separated by $(n_1/n_2)a$.

We have taken nmr and esr spectra of a series of phenoxy and nitroxide radicals shown in Figure 1. The nmr and esr spectra of the phenoxy monoradicals were also taken. Susceptibility measurements were made on all of the biradicals except compound III which was too unstable for this type of measurement. Both the contact shifts and the susceptibility shifts were mea-

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[1] NSF Graduate Trainee, 1966–1968; NDEA Graduate Fellow, 1968–1969.

[2] R. W. Kreilick, *Mol. Phys.*, **14**, 495 (1968); *J. Amer. Chem. Soc.*, **90**, 5991 (1968); F. Yamauchi and R. W. Kreilick, *ibid.*, **91**, 3429 (1969); W. G. Espersen and R. W. Kreilick, *Mol. Phys.*, **16**, 577 (1969).

[3] W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, **87**, 3779 (1965).

[4] D. F. Evans, *J. Chem. Soc.*, 2003 (1959); E. DeBoer and C. MacLean, *J. Chem. Phys.*, **44**, 1334 (1966).

[5] C. P. Slichter, *Phys. Rev.*, **99**, 479 (1955); D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, 33, 700 (1960).

Table I. Nmr Shifts, Coupling Constants and Singlet–Triplet Separations for the Phenoxy Radicals at 297°K

Radical	Group	Shift,[a] kHz	$\chi_m \times 10^3$	*a*, G (nmr)	*a*, G (esr)	Δ*G*, kcal	Δ*S*, eu	Δ*H*, kcal	*D*, G
I mono	*t*-Butyl	0.37 ± 0.03	1.25[b]	+0.049					
I mono	*meta*	9.5 ± 0.4	1.25	+1.27	1.3				
I bi	*t*-Butyl	0.72 ± 0.02	3.0 ± 0.2	+0.041		−1.2 ± 0.4[c]	2.18[d]	−0.55	30
I bi	*meta*	16.5 ± 0.5	3.0 ± 0.2	+0.93	0.86	−1.9 ±0.4[e]	2.18	−1.32	
II mono	*meta*	10.0 ± 0.4	1.25	+1.34	1.36	+0.41 ±0.04[c]			
II bi	*t*-Butyl	0.16 ± 0.01	1.12 ± 0.05	+0.025		+0.37 ± 0.05[f]	3.3	+1.35	110
II bi	*meta*	4.75 ± 0.2	1.12 ± 0.05	+0.72					
III mono	*meta*	13.2 ± 0.4	1.25	+1.77	1.76				
III bi	*meta*	7.8 ± 0.3				+0.13 ±0.05[e]	2.18	+0.78	60

[a] Shifts are from the corresponding peaks in the diamagnetic phenols. [b] Susceptibilities calculated assuming Curie law behavior. [c] Determined from the susceptibility by eq 2. [d] Contribution to the entropy from differences in electronic degeneracies. [e] Determined from predicted coupling constant and the contact shift by eq 3. [f] Determined from the temperature dependence of the contact shift.

sured at a series of different temperatures. Coupling constants and singlet–triplet separations were determined for the phenoxy biradicals. The spectra of the nitroxide biradicals indicated that $RT \gg \Delta G$ for these compounds, and we were only able to determine the coupling constants.

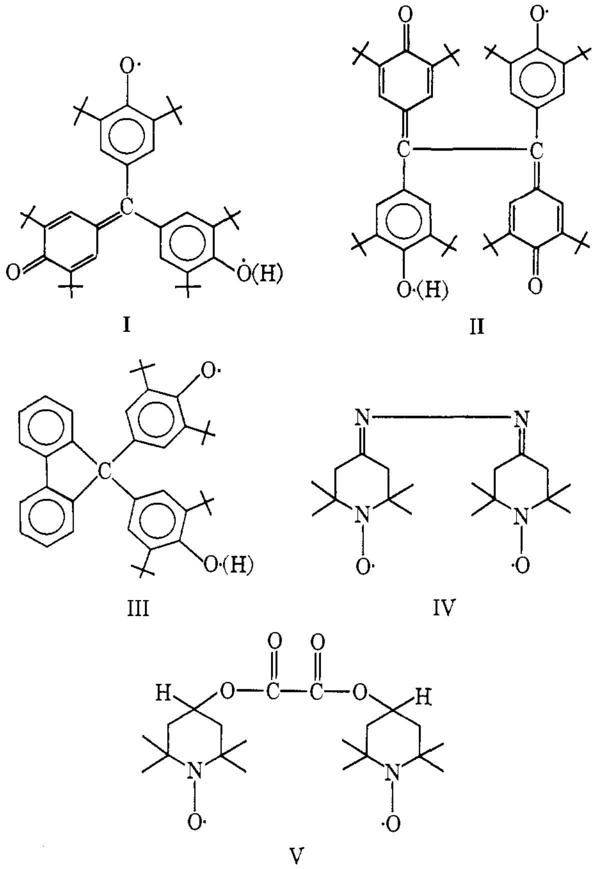

Figure 1. Compounds investigated.

Experimental Section

(1) **Compounds.** Bis(phenol) I was prepared by the method of Yang and Castro.[6] Bis(phenol)s II and III were kindly provided by Dr. E. A. Chandross.[7,8] The two nitroxide biradicals IV and V were prepared by the method of Briere, *et al.*[9] The phenoxy biradicals were made by oxidizing a benzene solution of the appropriate phenol with aqueous alkaline $K_3Fe(CN)_6$. The benzene layer was washed with a solution of K_2CO_3, dried on K_2CO_3, and evaporated. When shorter oxidation times were used, we were able to obtain the monoradicals. The biradicals were stable in the solid state. Biradicals I, II, and IV decomposed slowly in solution, while biradical III decomposed over the period of a few hours.

When nmr samples were made in $CDCl_3$ or CS_2, we were able to observe the nmr peaks with smaller shifts. When DBNO was used as the solvent, we were able to observe all of the peaks except those which were overlapped with the DBNO line. The spectra contained lines from diamagnetic impurities which were used as internal reference peaks.

(2) **Instruments.** The nmr spectra were taken on a JEOLCO 4H-100 100-MHz nmr spectrometer equipped with a broad-line unit employing 35-Hz field modulation. Esr spectra were taken on a JEOLCO 3BSX esr spectrometer.

(3) **Susceptibility Measurements.** The susceptibilities of the radicals were determined by measuring the shift of the tetramethylsilane (TMS) peak in a solution of a given radical from the TMS line in a diamagnetic solvent.[4] Measurements were made by interchanging samples of various radical concentrations with a sample which contained only the solvent and TMS. The accuracy of this technique was checked by measuring the susceptibilities of a series of monoradicals of known concentration. The experimental susceptibilities were generally within 3% of the theoretical values.

These measurements were made on either a JEOLCO 4H-100 spectrometer, a JEOLCO C-60H spectrometer, or a Varian A-60 spectrometer. Variable-temperature measurements were conducted on the latter two instruments to minimize the problem of field drift. In order to obtain values for the susceptibilities, one must know the concentration of radical in the samples. Our samples generally contained some diamagnetic impurities. We determined the per cent impurity by integrating the nmr lines from the impurities and a line from the biradicals and comparing areas. This procedure introduced some error into our values for the susceptibilities because of inaccuracies in the integrals of the broad lines which were observed.

Results and Discussion

We were able to observe lines from the *t*-butyl and aromatic protons in the nmr spectra of most of the phenoxy mono- and biradicals. The *t*-butyl line from compound III was obscured by peaks from diamagnetic impurities. The spectra of the nitroxide biradicals showed peaks from the methyl and methylene protons. The shifts and coupling constants are listed in Table I. Data from susceptibility measurements and esr spectra are also given in this table.

Compound I. The esr spectrum of biradical I shows seven lines from the interaction of the electrons with the six aromatic protons.[10] The coupling constant of 0.86 G is nearly two-thirds of the coupling observed from monoradical I. This behavior is expected when each of the electrons interacts with all of the nuclei ($J \gg a$).

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[6] N. C. Yang and A. J. Castro, *J. Amer. Chem. Soc.*, **82**, 6208 (1960).

[7] E. A. Chandross, *ibid.*, **86**, 1263 (1964).

[8] E. A. Chandross and R. W. Kreilick, *ibid.*, **86**, 117 (1964).

[9] R. Briere, R. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, **32**, 3290 (1965).

[10] R. W. Kreilick, *J. Chem. Phys.*, **43**, 308 (1965).

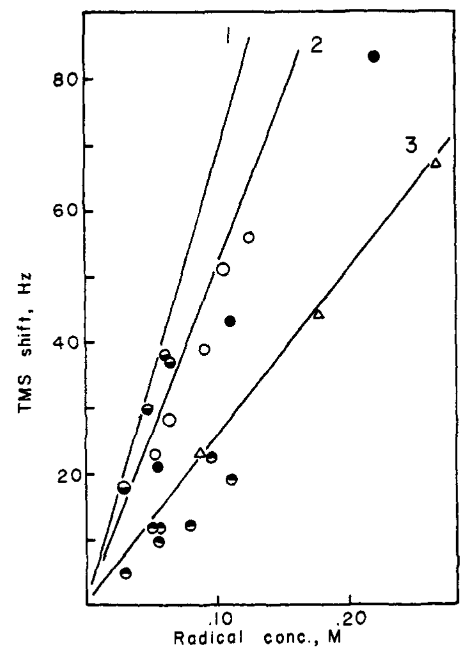

Figure 2. Susceptibility shifts for the biradicals at 297°K: (1) theoretical line for pure triplet; (2) theoretical line for a biradical with $RT >> \Delta H$; (3) theoretical line for a doublet. ◒, biradical I; ◓, biradical II; ○, biradical IV; ●, biradical V; △, 4-hydroxy nitroxide monoradical.

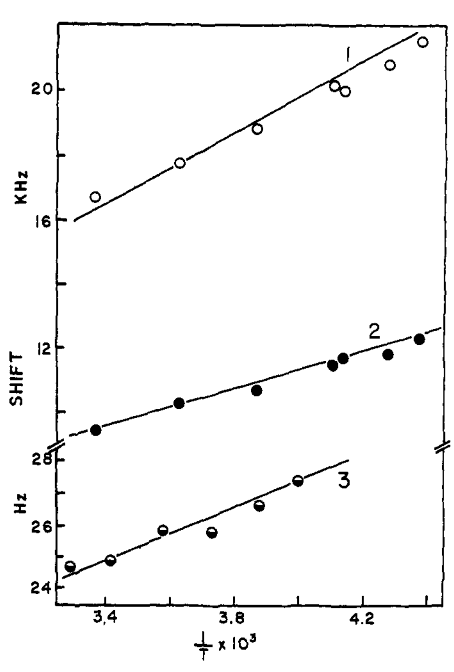

Figure 3. *meta* proton contact shifts and TMS susceptibility shift *vs.* the reciprocal of temperature: (1, 3) theoretical lines for $\Delta H = -0.55$ kcal/mole and $\Delta S = 2.18$ eu; (2) theoretical line for Curie law dependence. ○, biradical I in DBNO; ●, monoradical I in DBNO; ◒, TMS shift in the presence of 0.04 *M* biradical I.

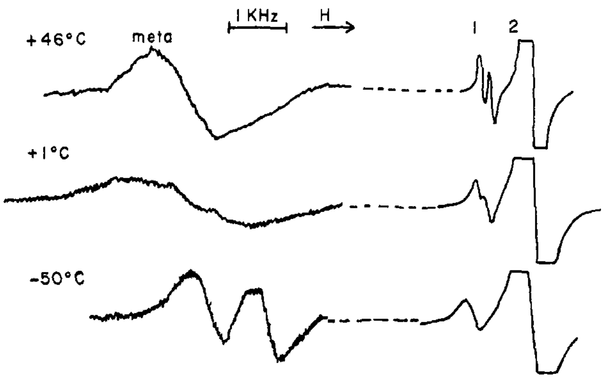

Figure 4. Nmr spectrum of biradical II at a series of temperatures: (1) radical *t*-butyl peak overlapped with diamagnetic *t*-butyl peak; (2) DBNO peak.

The coupling constant which was calculated from the shift of the monoradicals *meta* proton nmr peak was identical with the value obtained from the esr spectrum. The shifts observed from the biradical were larger than those from the monoradical but smaller than the shifts expected from a pure triplet. These data indicate that the biradical is a ground-state triplet with a thermally accessible singlet state. A molecular orbital calculation carried out by Kearns and Ehrenson has predicted that this molecule should be a ground-state triplet.[11]

The susceptibility data are consistent with this interpretation. A plot of susceptibility shifts *vs.* concentration is given in Figure 2. The line from biradical I is slightly below the line predicted for a pure triplet. When the susceptibility and contact shift were introduced into eq 1 and 2, we obtained values of -1.20 kcal for ΔG and $+0.93$ G for the *meta* proton coupling constant. When the coupling constant determined from the esr spectrum was introduced into eq 3, we obtained a ΔG of -1.97 kcal. The difference in these values probably reflect errors in our susceptibility measurements.

The contact shifts and the susceptibility varied linearly with the reciprocal of temperature (Figure 3). This behavior was expected as ΔG is negative and the exponential term in eq 3 is small. If the entropy difference between the singlet and triplet states is associated solely with the difference in electronic degeneracies, one predicts that $\Delta S = R \ln 3 = 2.18$ eu. This value can be combined with ΔG to give the enthalpy difference between the singlet and triplet states (Table I).

Compound II. The esr spectrum of biradical II consisted of a single broad line.[7] The monoradical spectrum showed five lines with a separation of 1.36 G. The coupling constant calculated from the shift of the monoradical's *meta* aromatic nmr line was identical with this. The lines in the nmr spectrum of the biradical were shifted less than those of the monoradical. Spectra of the biradical at a series of temperatures are shown in Figure 4. The susceptibility of this compound was well below that predicted for a pure triplet. The contact shift and susceptibility data indicate that this biradical is a ground singlet with a thermally accessible triplet state. Our susceptibility data show that about 32% of the molecules are in the triplet state at room temperature. We obtained values of 0.41 kcal for ΔG and 0.72 G for the *meta* coupling constant when we introduced the contact shift and the susceptibility data into eq 1 and 2. The *meta* proton coupling constant is predicted to have a value of 0.67 G if J is greater than a. The predicted value for the *t*-butyl protons is 0.023 G, and the observed value is 0.025 G. When the predicted coupling constants were introduced into eq 3, we obtained a value of 0.36 kcal for ΔG.

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(11) D. Kearns and S. Ehrenson, *J. Amer. Chem. Soc.*, **84**, 739 (1962).

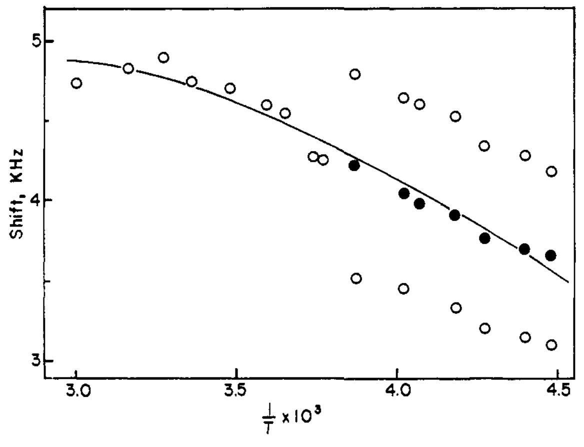


Figure 5. Shift of the *meta* proton line of biradical II *vs.* the reciprocal of temperature: ○, experimental points; ●, average value of high- and low-field lines. The solid line is the theoretical line calculated from eq 3 with $a = 0.068$ G, $\Delta H = 1.35$ kcal/mole, and $\Delta S = 3.3$ eu.

We measured the susceptibility shifts, the *t*-butyl proton contact shift, and the aromatic proton contact shift at a series of temperatures. The data from the susceptibility measurements and the *t*-butyl proton contact shift were rather inaccurate because of the small changes observed over the accessible temperature range. These data qualitatively confirmed that this biradical is a ground singlet as the *t*-butyl shift and the susceptibility increased with increasing temperature.

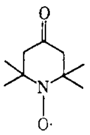
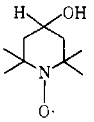
The data from the *meta* proton peak was more accurate, and an estimate of the singlet–triplet separation could be made from the temperature dependence of this shift. The *meta* proton peak was split into two separate lines of intensity 1:1 at temperatures below −10° (Figure 4). The two lines were positioned at equal distances on the high- and low-field side of the predicted position of the original peak. Apparently the *meta* protons become magnetically nonequivalent at lower temperatures and have different coupling constants. This behavior may be associated with hindered rotation about the aromatic methylene bonds. If this is the case, the low-temperature spectra can be explained if the molecules are locked in a given conformation in which the aromatic protons are magnetically nonequivalent. A similar effect has been observed in the endor spectra of a number of galvinoxyl derivatives.[12]

A plot of the *meta* proton shift *vs.* the reciprocal of temperature is shown in Figure 5. This plot was fitted with a nonlinear least-squares computer program[13] which analyzed the data in terms of eq 3. We assumed that the coupling constant was 0.67 G and calculated ΔH and ΔS. The free-energy separation between the singlet and triplet states was determined to be 0.37 kcal at 297°K and the entropy difference was 3.3 eu. This value for the entropy is slightly greater than that expected from the difference in electronic degeneracies.

Compound III. Biradical III was rather unstable, and we were unable to determine either the susceptibility or the temperature dependence of the contact shifts. The *t*-butyl peaks from both the mono- and biradicals were obscured by diamagnetic impurity lines. Lines from the *meta* protons were observed in the spectra of both the mono- and biradicals. The coupling constant calculated from the line in the nmr spectrum of the monoradical was identical with our esr result (1.76 G). The esr spectrum of the biradical consisted of a single broad line. The shift of the *meta* proton line in the nmr spectrum of the biradical was less than that observed from the monoradical. This behavior indicates that this biradical is a ground-state singlet with a thermally accessible triplet state. If one assumes that the coupling constant of the biradical is one-half of the value observed from the monoradical, it is possible to use eq 3 to calculate ΔG. We obtain a singlet–triplet separation of 0.13 kcal with this technique.

Compound IV. The esr spectrum of nitroxide biradical IV shows the five-line pattern expected from a molecule in which the electrons interact with two equivalent nitrogens. This behavior is predicted for cases in which J is greater than a. We were unable to obtain the nmr spectrum of the monoradical and therefore cannot directly compare the proton couplings of the one- and two-electron species. As an alternative, we have compared the shifts in the spectrum of the biradical to those of a monoradical of similar structure. The monoradical which has been used contains a carbonyl group at the 4 position[14] rather than the azine group (Table II). The shifts observed from biradical IV were almost identical with those observed from this monoradical. One predicts identical shifts from one- and two-electron species in cases in which the enthalpy difference between the singlet and triplet states is much less than RT. When this is the case, the nmr spectra from

Table II. Nmr Shifts and Coupling Constants for the Nitroxide Radicals at 297°K

Radical	Group	Shift,[a] kHz	a, G[b] (nmr)	a, G (esr)
	CH_3	0.89	−0.12	0.09
	CH_2	0.12	−0.015	
	N			14.2
IV	CH_3	0.89	−0.06	
	CH_2	0.08	−0.006	
	N			7.34
	$CH_3(\alpha_1)$	2.70	−0.36	
	$CH_3(\alpha_2)$	0.16	−0.02	
	$CH_2(\beta_1)$	2.29	−0.31	
	$CH_2(\beta_2)$	3.56	−0.48	
	$CH(\gamma)$	0.53	+0.07	
	N			15.2
V	$CH_3(\alpha_1)$	2.91	−0.20	
	$CH_3(\alpha_2)$	0.12	−0.008	
	$CH_2(\beta_1)$	2.14	−0.15	
	$CH_2(\beta_2)$	3.43	−0.24	
	$CH(\gamma)$	0.62	+0.04	
	N			15.2

[a] The shifts are from the corresponding peaks in the diamagnetic amines. [b] The coupling constants for the biradicals were calculated with the assumption that $J \gg a$.

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(12) C. Steelink, J. Fitzpatrick, L. Kispert, and J. S. Hyde, *J. Amer. Chem. Soc.*, 90, 4354 (1968).

(13) This program was written by Professor L. D. Colebrook of this department to whom acknowledgment is made.

(14) R. W. Kreilick, *J. Chem. Phys.*, 46, 4260 (1967); R. Briere, H. Lemaire, A. Rassat, P. Rey, and A. Rousseau, *Bull. Soc. Chim. Fr.*, 4479 (1967).

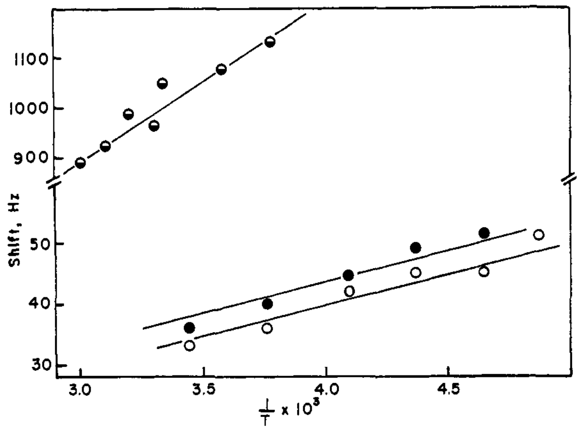

Figure 6. Methyl proton contact shift and TMS susceptibility shift *vs.* the reciprocal of temperature: ⊖, methyl protons in biradical IV; ●, TMS shift in the presence of 0.09 *M* biradical V; ○, TMS shift in the presence of 0.09 *M* biradical IV. The lines represent the predicted behavior when $\Delta H \ll RT$.

biradicals with $J \gg a$ should be identical with the spectra from biradicals with $J \ll a$. The esr spectrum of biradical IV indicated that J is greater than a. We have assumed that this was the case when calculating the coupling constants listed in Table II.

The temperature dependence of the methyl proton shift and the susceptibility shift are shown in Figure 6. These shifts varied linearly with the reciprocal of temperature over the region investigated. Variable-temperature esr measurements were made on a sample of biradical IV doped with DBNO. The relative intensities of lines from the mono- and biradical remained constant down to −40°. At this point the lines in the spectrum of the biradical began to broaden, and accurate measurements were impossible. All of these data indicate that ΔH is less than RT for this biradical.

Compound V. Glarum and Marshall have reported that the value of J for nitroxide biradical V is about 5 G at room temperature.[15] This value is less than the nitrogen coupling constant but greater than the proton coupling constants. We were unable to observe the nmr spectrum of monoradical V and have compared the biradical spectrum with that of a monoradical with a hydroxy group in the 4 position[14] (Table II). The shifts from biradical V and this monoradical were almost identical, indicating that $\Delta H \ll RT$. The temperature dependence of the susceptibility (Figure 6) also indicated that $\Delta H \ll RT$. We calculated the coupling constant given in Table II with the assumption that J is greater than the proton coupling constants. Our data do not distinguish between this case and the case in which the two ends of the molecule act as separate monoradicals. If the latter were the case, the coupling constants would have twice the values of those given in Table II.

In a recent paper, Brinen and Orloff have noted a linear correlation between the zero-field splitting parameter D and the singlet–triplet separation for a number of aromatic hydrocarbons.[16] Figure 7 shows a plot containing the data which they have reported and our data for the phenoxy biradicals. Our data appear to fall on the same line as that obtained for the phosphorescent triplets.

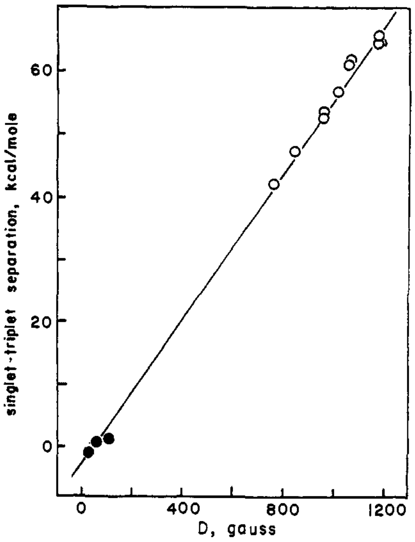

Figure 7. Singlet–triplet enthalpy separation *vs.* zero-field splitting parameter: ●, our data; ○, data from ref 16.

Conclusion

We have taken the nmr spectra and measured the susceptibilities of a number of stable organic biradicals. Electron–nuclei coupling constants were calculated from these data. In some instances we were able to determine the energy separation between the singlet and triplet states. Biradical I was found to be a ground-state triplet while biradicals II and III were found to be ground-state singlets. The enthalpy difference between the singlet and triplet states in the two nitroxide biradicals (IV and V) was found to be less than RT.

The singlet–triplet separations of these biradicals should reflect the magnitude of the electron–electron exchange integral. The phenoxy biradicals were observed to have larger singlet–triplet separations than the nitroxides. This behavior might have been expected as the phenoxy biradicals are conjugated while the electrons are largely localized on the N–O groups in the nitroxide biradicals. The two ends of the nitroxide biradicals probably have to be relatively close together for the molecular orbitals to overlap effectively. It is interesting that our values for singlet–triplet separations and zero-field splitting parameters fell on the same line as the values for the phosphorescent triplets.

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(15) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967).

(16) J. S. Brinen and M. K. Orloff, *Chem. Phys. Letters*, **1**, 276 (1967).