from which we obtain

$$[A]_\infty - [A]_t = \frac{k_1[AO_2]_0}{k_1 + k_2[C]} e^{-(k_1 + k_2[C])t}$$

and

$$\ln([A_\infty] - [A]_t) = \ln \frac{k_1[AO_2]_0}{k_1 + k_2[C]} - (k_1 + k_2[C])t$$

The values of $k_1 + k_2[C]$ obtained in this way (Figure 11) were found to agree with values derived from the decay of chemiluminescence (squared point in Figure 8).

A high-resolution mass spectrum of the product obtained in acidified dioxane is in agreement with the structure proposed by Rigaudy[1e] and Baldwin, *et al.*[5]

We are also investigating the decomposition of 1,4-dialkoxy-9,10-diphenylanthracene peroxides in benzene, where a nonreversible reaction occurs apparently without the action of acid or other reactants. This nonreversible reaction appears to be responsible for the generation of light.

Electron Spin Resonance Studies of Nitroxide Radicals and Biradicals in Nematic Solvents[1a]

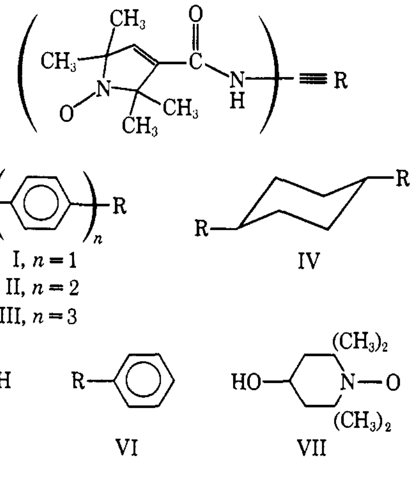
Carlo Corvaja, Giovanni Giacometti, Kenneth D. Kopple,[1b] and Ziauddin

Contribution from the Institute of Physical Chemistry, University of Padua, Padua, Italy, and the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. *Received September 20, 1969*

Abstract: Electron spin resonance spectra of a series of nitroxide radicals and biradicals in the nematogenic solvents *p*-azoxyanisole and *p*-butyloxybenzoic acid have been examined. Three of the biradicals constitute a series of rigid molecules of graduated length between nitroxide groups. The observed nitrogen hyperfine splittings were used to determine the orientation of the solutes in the liquid crystal. The degree of orientation increases with increasing molecular length and is consistent with the observed electron–electron dipolar splittings where these were observed.

Use of liquid crystal solvents for electron spin resonance studies of organic radicals and biradicals has recently received much attention.[2–7] In this paper we report the spectra in both isotropic and nematic solvents of the series of nitroxide biradicals I–IV, which are molecules with graduated, approximately fixed spacings between radical sites. The isotropic spin exchange coupling between the radical sites in these molecules is small, but they also provide a series of rigid radicals of graduated lengths that can be used for an investigation of the effect of chain length on the orientation of molecules in liquid crystal phases. A quantitative study of this kind of orientation has recently been reported by Ferruti, *et al.*,[7] using one nitroxyl radical with a long flexible tail. For comparison we have also examined the behavior of analogous monoradicals, V and VI, in nematic solvents.

Numerous bis(nitroxide) radicals have already been prepared. Most extensively studied have been esters of the alcohol VII with dibasic acids. Esr spectra of such molecules in isotropic solvents indicate that flexibility that permits the radical sites to approach each other is necessary if there is to be strong ($J \gg a_N$) spin exchange coupling between sites.[8–11] For example there is strong coupling in the succinate ester[9] but none in the terephthalate.[8,10] Spectra of the carbonate,[6,9] glutarate,[3] and terephthalate[3] have also been examined in nematic solvents. The biradicals we now report on are more rigid than these, in that the potentially flexible six-membered ring is replaced by a rigid five-membered



I, *n* = 1
II, *n* = 2
III, *n* = 3
IV
V
VI
VII

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(1) (a) Supported by the National Research Council of Italy (Chemistry Committee) and the National Science Foundation, Grant No. GP 6779; (b) address correspondence to this author at Illinois Institute of Technology.

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(10) E. G. Rozantsev, V. A. Golubev, M. B. Nieman, and Yu. V. Kokhanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 572 (1965).

(11) E. G. Rozantsev, G. F. Pavelko, A. L. Buchachenko, and M. B. Nieman, *ibid.*, 2306 (1967).

Table I. Analyses of 2,2,5,5-Tetramethylpyrroline-1-oxyl-3-carboxamides

Compound	Mp, °C[a]	Empirical formula	Calculated, %			Found,[b] %		
			C	H	N	C	H	N
I	267 dec	$C_{24}H_{32}N_4O_4$	65.43	7.32	12.72	65.24	7.42	12.73
II	241 dec	$C_{30}H_{36}N_4O_4$	69.74	7.02	10.85	70.00	7.04	10.82
III	259–260	$C_{36}H_{40}N_4O_4$	72.95	6.80	9.45	72.58	7.01	9.80
IV	278 dec	$C_{24}H_{38}N_4O_4$	64.54	8.58	12.55	63.93	8.49	12.00
V	166	$C_{16}H_{19}N_2O_2$	69.53	7.33	10.81	68.97	7.49	11.00

[a] Melting points corrected. [b] Analyses by Micro-Tech Laboratories, Skokie, Ill.

one, and the ester group is replaced by the more rotationally constrained monosubstituted amide, and the distance between the odd electron dipoles thus is known with more certainty.

Dreiding molecular models of I, II, and III indicate that the distance between the two nitroxide nitrogens is virtually independent of rotation about the single bonds in these biradicals, provided the amide groups remain *trans* and planar. Studies of monosubstituted amides in solution or the liquid state[12] as well as in crystalline form[13] have shown that they are, in fact, preferentially *trans* and planar. From the models, the N–N distances are for I, 15; for II, 19.2; and for III, 23.6 Å, within an uncertainty of 0.3 Å. The 1,4-cyclohexylene biradical IV was prepared to compare the effects of saturated and unsaturated (I) spacing moieties. It has the same N–N distance as I, if both of the acylamino groups are equatorially substituted on the chair form of the cyclohexane ring; since any other conformation is unlikely, the spectra of IV in nematic solvents were not investigated.

Experimental Section

Materials. 2,2,5,5-Tetramethylpyrroline-1-oxyl-3-carboxamide (VI) and 2,2,5,5-tetramethylpyrroline-1-oxyl-3-carboxylic acid were prepared according to Rozantsev and Krinitzkaya.[14] *trans*-1,4-Diaminocyclohexane[15] and 4,4′′-diamino-*p*-terphenyl[16] were also prepared according to the literature methods. The new derivatives described in this report (I–IV) were prepared from tetramethylpyrroline-1-oxyl-3-carbonyl chloride as described below.

p-Azoxyanisole (PAA) was a Fluka product and was used without further purification; *p*-*n*-butyloxybenzoic acid (PBB) was prepared according to a method described in the literature.[17]

2,2,5,5-Tetramethylpyrroline-1-oxyl-3-carbonyl Chloride. A mixture of the corresponding carboxylic acid[14] (6.3 g, 0.0342 mol) and phosphorus pentachloride (9.6 g, 0.426 mol) in 800 ml of 1:1 toluene–light petroleum (60–80°) was stirred for 6 hr at 35°. Additional phosphorus pentachloride (1 g) was added after 6 hr, and stirring was continued for 2 hr. The resulting bright yellow solution was filtered and evaporated to dryness under reduced pressure to give an orange oil that was taken up in 500 ml of dried (calcium hydride) *n*-hexane and again filtered. The hexane was removed under reduced pressure to give an orange liquid product assumed to be the acid chloride; this was not further purified. Its infrared spectrum (neat oil) showed a carbonyl stretching absorption at 1750 cm^{-1}, the initial carboxylic acid absorbing at 1630 cm^{-1} (potassium bromide pellet).

Preparation of Amides I–V. A methylene chloride solution of the crude acid chloride just described, containing 1.5–2 molar equivalents for each amino group to be acylated, was added to a vigorously stirred chloroform–water (2:1) mixture containing the amino component and excess sodium carbonate (4–5 formula equivalents). Stirring was continued for about 8 hr and then the organic phase was separated, washed with 0.5 *N* hydrochloric acid and with water, and dried over anhydrous sodium sulfate. The chloroform solution was then freed of dark-colored by-products by passing it through a column of neutral Woelm alumina, eluting with additional chloroform all of the bright yellow nitroxyl derivative. The eluate was evaporated to dryness and repeatedly recrystallized from acetone–water (for III, acetic acid–ethanol was used). Analytical data are given in Table I. All of the compounds exhibited amide I bands in the 1650–1670-cm^{-1} region of the infrared (potassium bromide pellets). Yields ranged between 10 and 30%.

Spectra. Electron spin resonance spectra were obtained on a Varian E-3 instrument (9.5 GHz) equipped with a E-4540 variable temperature accessory. Samples were prepared by sealing standard quartz tubes under a pressure of about 10^{-2} mm. This was sufficient to eliminate oxygen, which is harmful both for the radicals and the solvents at the elevated temperatures used.

Spectra of the radicals in the liquid crystal solvents were measured at temperatures between 110 and 145° for *p*-azoxyanisole (PAA) and between 135 and 175° for *p*-*n*-butyloxybenzoic acid (PBB). PAA melts at 118° to a nematic phase and has a nematic–isotropic transition at 135°. PBB melts at 146° and becomes isotropic at 165°. Spectra were measured at intervals of 5° and reversibility of behavior was established.

Results

Electron spin resonance spectra of I–III, about 10^{-5} *M*, are shown in Figure 1. Biradical I exhibits a weak spin exchange interaction, about 2.5 G, temperature independent between −60 and 80°. There is no visible *J* splitting in the spectra of the more extended biradicals II and III. Also, biradical IV, which has about the same fixed distance between nitroxyl groups as I, shows no detectable evidence of such interaction.

The spectra measured in the liquid crystal solvents PAA and PBB at temperatures above the nematic–isotropic transition, although somewhat broadened, are otherwise identical with those of solutions in ordinary solvents.

In the nematic solvents the biphenylene radical II and the cyclohexylene biradical IV exhibit splitting due to electron–electron dipolar coupling; a *D* splitting of 3.7 G (160° in PBB), as shown in Figure 2, appears for II and one of 3.0 G (120° in PAA) has been measured for IV. For the terphenylene biradical, III, there is observed only increased line width on going from isotropic to nematic phases. Surprisingly, the observed spectra of the phenylene biradical, I, an example of which is shown in Figure 3, do not exhibit structure clearly attributable to *D* or *J* splittings.

The nitrogen hyperfine splittings in the nematic phases differ from the values in isotropic solvents, and vary with temperature as shown in Tables II and III. The hyperfine coupling constant, a_N, decreases suddenly on going from isotropic to nematic phases and continues decreasing in the latter as the temperature is lowered. This occurs both with the biradicals I–III and the monoradicals V and VI. The difference

$$\Delta a_N = a_N^{\text{iso}} - a_N^{\text{nem}} \quad (1)$$

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(12) L. A. Laplanche and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 337 (1964), and ref 5–12 cited therein.

(13) R. E. Marsh and J. J. Donohue, *Advan. Protein Chem.*, **22**, 235 (1967).

(14) E. G. Rozantsev and L. A. Krinitzkaya, *Tetrahedron*, **21**, 491 (1965).

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(16) J. A. VanAllen, *ibid.*, **21**, 1152 (1956).

(17) A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 2661 (1929).

Table II. Temperature Dependence of Nitrogen Hyperfine Coupling of Nitroxides in *p*-Azoxyanisole

I	Temp, °C	145	140	130	124	120	110		
	a_N	14.75	14.75	13.25	13	12.9	13		
	$-\Delta a_N/A_\perp'$			0.16	0.18	0.19	0.18		
II	Temp, °C	145	140	135	130	125	120	116	110
	a_N	14.85	14.85	12.6	12.2	11.9	11.6	11.2	10.85
	$-\Delta a_N/A_\perp'$			0.22	0.26	0.30	0.33	0.37	0.41
III	Temp, °C	150	135	130	125	120	115	110	
	a_N	14.85	14.85	11.72	11.25	10.9	10.6	10.6	
	$-\Delta a_N/A_\perp'$			0.32	0.37	0.41	0.43	0.44	
V	Temp, °C	145	140	135	130	125	120	115	
	a_N	14.8	14.8	14.2	14	13.9	13.8	13.75	
	$-\Delta a_N/A_\perp'$			0.06	0.08	0.09	0.10	0.11	
VI	Temp, °C	140	135	130	125	120	115	110	
	a_N	14.85	14.85	13.55	13.25	13.1	12.95	12.75	
	$-\Delta a_N/A_\perp'$			0.13	0.16	0.17	0.19	0.21	

increases, in both nematic solvents, with increasing molecular length. An exception is monoradical V in PBB, for which Δa_N is larger than expected on this basis alone. In PBB, for all of the compounds, a_N shifts to slightly above the isotropic value on cooling to about 150°.

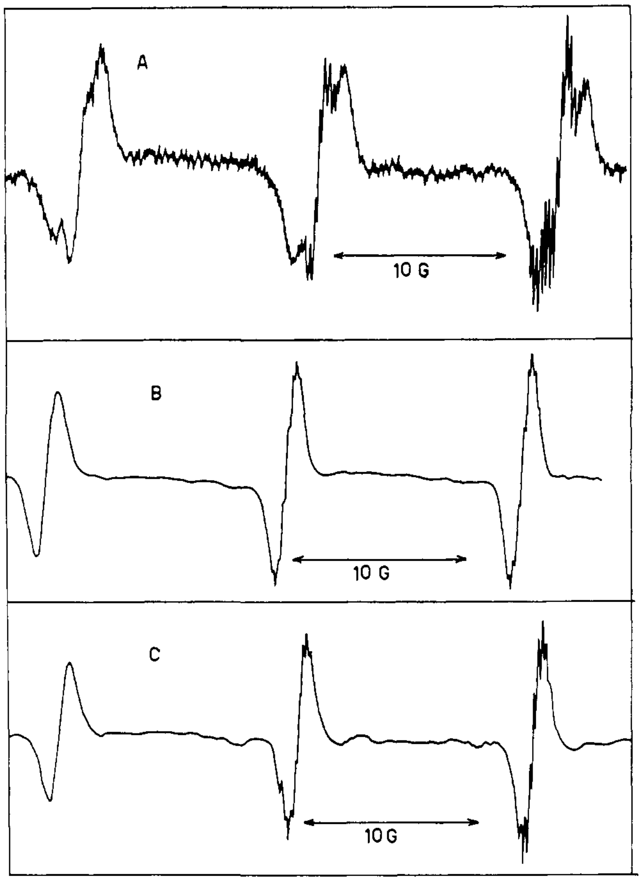

Figure 1. Esr spectra at 20° in isotropic solvents. Magnetic field increases to the left: A, I in benzene, about 5×10^{-6} *M*; B, II in toluene, about 10^{-4} *M*; C, III in toluene, about 3×10^{-5} *M*.

Discussion

The nematic state of ordered liquids has been described in terms of two models, the "swarms" theory and the distortion hypothesis. What is essential to explain esr effects in solvents of this kind is the idea that the molecules of the liquid are preferentially oriented (in particular domains according to the first model, and throughout the liquid according to the second), and that this orientation induces an orientation in the molecules of the solute. The anisotropic fine and hyperfine coupling tensors, as well as the *g* tensor, are not then averaged out. It is impossible to discriminate between the two models on the basis of measurement of these tensors[18] although a possibility in this direction may arise from relaxation effects.[19]

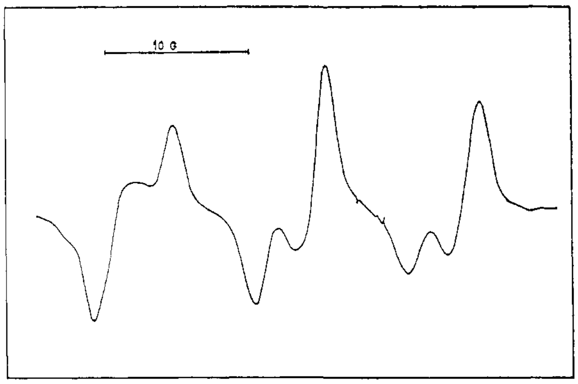

Figure 2. Esr spectrum of II in PBB at 160°.

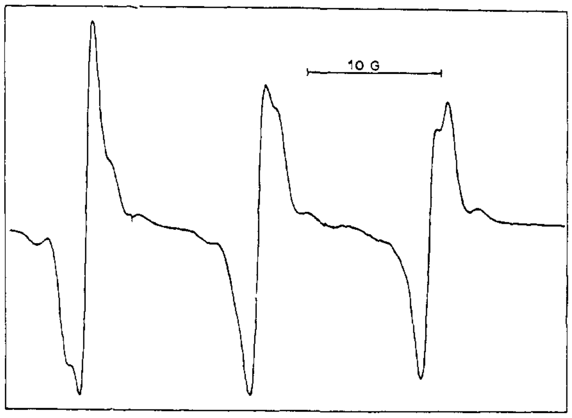

Figure 3. Esr spectrum of I in PAA at 120°.

The partial orientation of the solute in a nematic liquid is described by factors S_{ij}, where S is the average

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(18) G. R. Luckhurst, *Mol. Cryst.*, 2, 363 (1967).

(19) Attempts along this line are currently being made by P. L. Nordio in these laboratories.

Table III. Temperature Dependence of Nitrogen Hyperfine Coupling of Nitroxides in *p*-Butyloxybenzoic Acid

I Temp, °C	175	170	165	160	155	150	145		
a_N	15	15	14.8	12.6	12.6	15.1	15.4		
$-\Delta a_N/A_\perp'$			0.02	0.24	0.24	−0.01	−0.04		
II Temp, °C	175	170	165	162	160	155	150	145	140
a_N	15.1	15.1	11.8	11.25	10.6	10.5	15.2	15.4	15.5
$-\Delta a_N/A_\perp'$			0.32	0.38	0.44	0.45	−0.01	−0.04	−0.05
III Temp, °C	175	170	165	160	155	150	145	135	
a_N	15.1	15.1	11.1	10.4	10.2	9.9	15.6	15.8	
$-\Delta a_N/A_\perp'$			0.39	0.46	0.48	0.51	−0.06	−0.08	
V Temp, °C	170	165	160	155	150	145			
a_N	15.1	15.1	12.5	11.9	11.5	15			
$-\Delta a_N/A_\perp'$			0.25	0.31	0.35	0			
VI Temp, °C	175	170	165	160	155	150	145		
a_N	15	15	14.8	13	12.6	15.4	15.4		
$-\Delta a_N/A_\perp'$			0.02	0.20	0.24	−0.04	−0.04		

orientation matrix of the solute molecule,[20] z is the magnetic field direction, i and j are molecular axes, and

$$S_{ij} = \frac{3\langle l_{zi}k_{zi}\rangle - \delta_{ij}}{2}$$

l's are direction cosines. In the case of our radicals we may assume planarity of the rings, as is evident from ^{13}C couplings for the five-membered ring nitroxides,[21] and that the magnetic field is parallel to the molecular plane of completely oriented molecules. Taking axes as in Figure 4, we also assume that our radicals are elongated enough to allow us to neglect orientational anisotropy in directions perpendicular to the long (a) axis, and we may then set for our solutes $S_{cc} = S_{bb}$. Since the orientation tensor is traceless

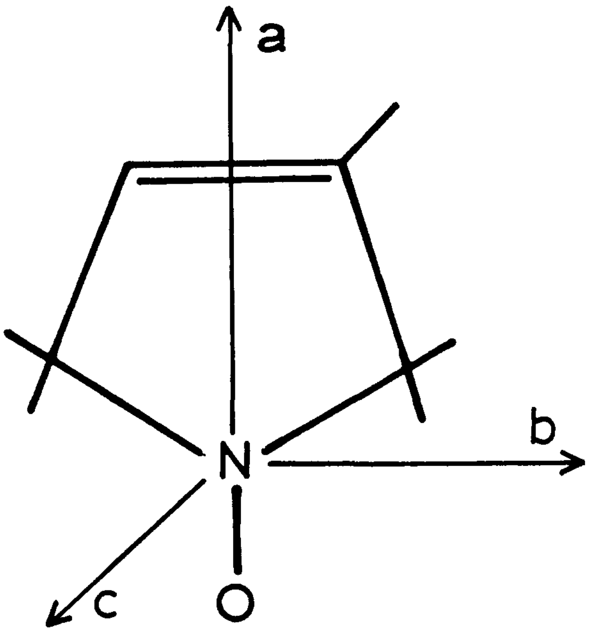
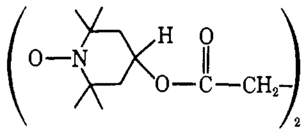


Figure 4. Molecular axes of nitroxides.

$$S_{aa} = -2S_{cc} \qquad (2)$$

Fine Structure Splittings. The p-phenylene biradical I shows only small, temperature-independent spin exchange coupling (2.5 G), and the similar, but nonaromatic cyclohexylene analog IV shows none. This is in contrast to the succinate ester VIII which has the same number of bonds between nitroxyl groups, but is



VIII

reported to show at room temperature an exchange coupling of over 50 G, which decreases with temperature with an activation energy of 3 kcal/mol.[9] Since I and IV are axially rigid, where VIII is flexible, this result confirms the suggestion of Rozantsev, *et al.*,[10] and Glarum and Marshall[9] that the dominant exchange mechanism in compounds like VIII is a direct process occurring in those conformations which bring the nitroxyl groups into proximity. There are no conformations of IV that bring the nitroxyls into juxtaposition; since $J \approx 0$ for this molecule, indirect exchange through the core of 13 σ bonds in IV or VIII is negligible. The small but observable coupling between unpaired electrons in I, however, indicates that some spin exchange can occur through an incompletely conjugated system of that length if the intervening groups are sufficiently susceptible.

For discussion of the dipolar splittings, the average dipolar Hamiltonian can be written

$$\langle\mathcal{H}\rangle_{\text{dip}} = \frac{2}{3}S_{ab}D_{ab}\mathbf{S}_{1z}\mathbf{S}_{2z} - \frac{1}{3}S_{ab}D_{ab}(\mathbf{S}_{1x}\mathbf{S}_{2x} + \mathbf{S}_{1y}\mathbf{S}_{2y})$$

Taking into account the assumed cylindrical symmetry for the elongated molecules, we can write

$$D_{bb} = D_{cc} = -D$$

$$D_{aa} = 2D$$

and

$$S_{ab}D_{ab} = S_{aa}2D - (S_{bb} + S_{cc})D$$

Hence

$$S_{ab}D_{ab} = 3DS_{aa}$$

and the average Hamiltonian becomes

$$\langle\mathcal{H}\rangle_{\text{dip}} = 2S_{aa}D\mathbf{S}_{1z}\mathbf{S}_{2z} - S_{aa}D(\mathbf{S}_{1x}\mathbf{S}_{2x} + \mathbf{S}_{1y}\mathbf{S}_{2y})$$

Therefore each line in the spectrum is split into two lines separated by $2DS_{aa}$ (provided the dipolar interaction is smaller than the hyperfine interaction).

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(20) A. Saupe, *Z. Naturforsch., A*, 19, 161 (1964).

(21) R. Brlere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965).

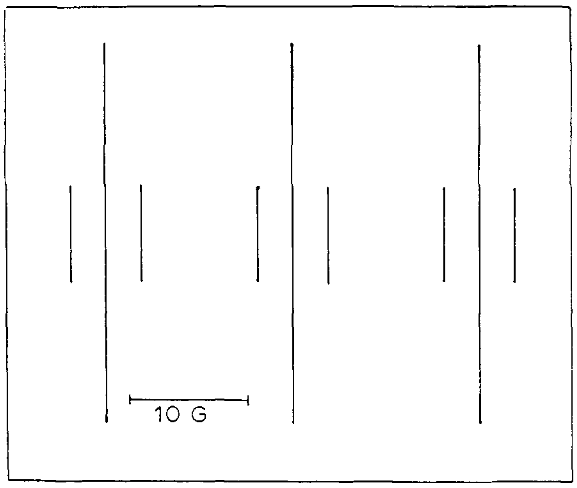

Figure 5. Pattern of esr spectrum of an oriented biradical with $A_{zz} = 16\,G, J = 4\,G, D_{zz} = -4\,G$.

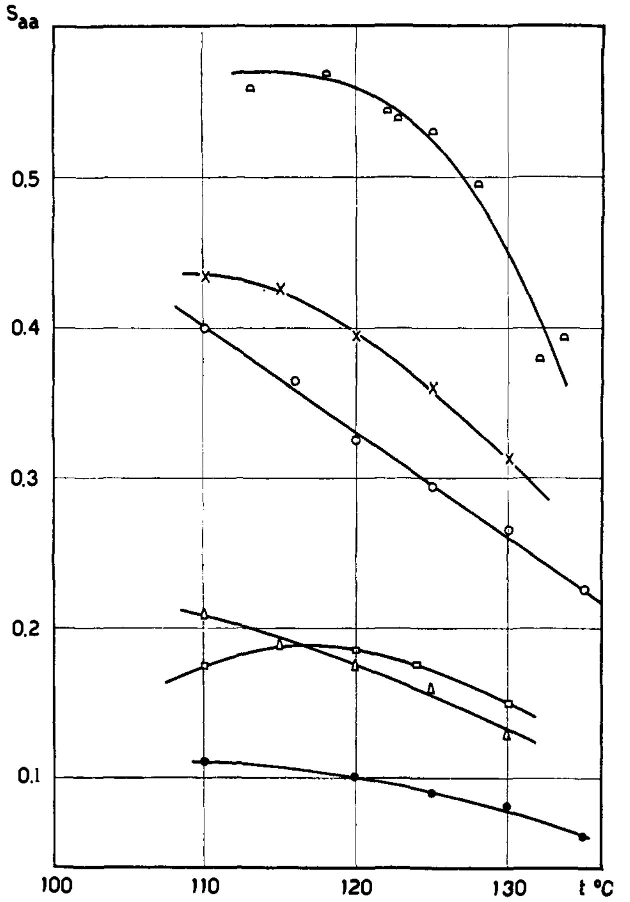

Figure 6. Orientation matrix element of PAA (□) and of nitroxide solutes in PAA (□, I; ○, II; ×, III; ●, V; △, VI).

Because of the large distance between the two radical sites, values of D can be calculated from the point-dipole approximation, as is done in Table IV. In the last two columns of Table IV, the maximum values of the observable splittings, $2DS_{aa}$, are calculated (for the two solvents) from the maximum S_{aa} values, determined from the hyperfine couplings as discussed below.

The observed dipolar splittings for radical II are in the expected range. For radical III, the line broadening in the nematic phase common to all cases (see, for example, Figure 2) makes it impossible to observe the smaller splitting.

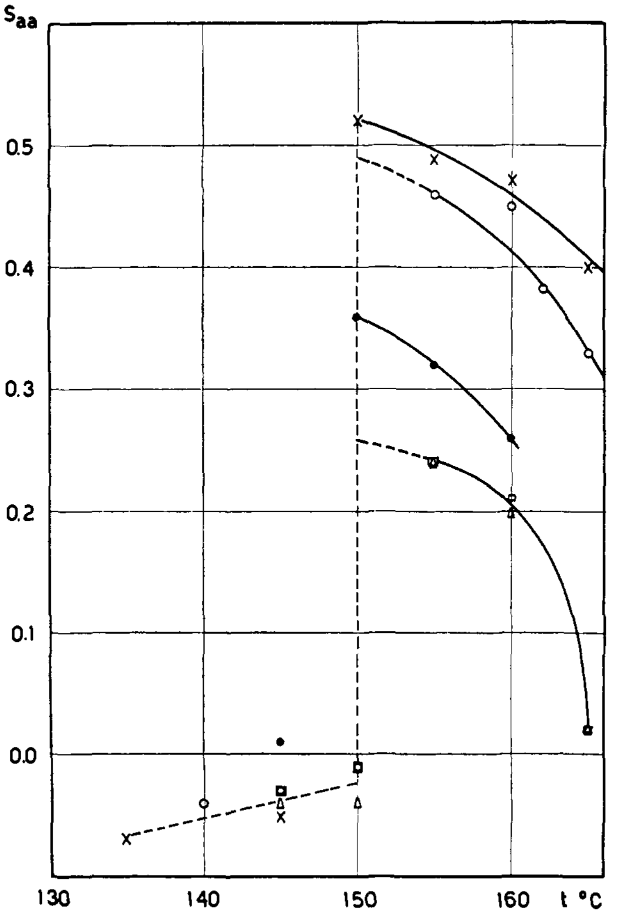

Figure 7. Orientation matrix element of nitroxide solutes in PBB (□, I; ○, II; ×, III; ●, V; △, VI).

For the spectra obtained with radical I (Figure 3), which do not show fine structure features, we do not have a satisfying explanation. This compound is the only one of the series in which the isotropic splitting, J, is of the same order of magnitude as the dipolar splitting, D. In such a case, the calculated spectrum must be obtained by complete diagonalization of the Hamiltonian, and unusual patterns may appear. To illustrate, Figure 5 shows the calculated spectrum for a case with integral ratios between coupling constants that are not unreasonable for I.

Table IV. Dipole-Dipole Splittings in Biradicals

Biradical	r, Å	D,[a] G	Splitting, G[b] PAA	PBB
I	15.0	8.2	3.2	4.0
II	19.2	3.9	3.2	3.6
III	23.6	2.1	1.8	2.2

[a] Calculated from the point-dipole approximation. [b] Calculated as $2S_{aa}D$; maximum values of S_{aa} taken from Tables II and III.

N Couplings in Nematic Phases. Assuming axial symmetry for the hyperfine coupling tensor $A(A_{aa} = A_{bb} = A_{\perp};\ A_{cc} = A_{\parallel})$, as shown in other cases for nitroxide radicals,[22] we can relate Δa_{N}, as defined in

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(22) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, 43, 2909 (1965).

(1), to S_{cc}

$$\Delta a_{\mathrm{N}} = 2S_{cc}A_{\perp}' \qquad (3)$$

where $A_{\perp}'$ is the perpendicular component of the traceless anisotropic tensor.

$$A_{\perp}' = A_{\perp} - A^{\mathrm{iso}} \qquad (4)$$

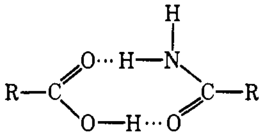
In Tables II and III values of $-\Delta a_{\mathrm{N}}/A_{\perp}'$ are collected by using a value for $A_{\perp}$ of 5 G, taken from ref 22. If we interpret these values, according to eq 2 and 3, giving the element S_{aa} of the average orientation matrix of our radicals, we may try to compare the results with analogous results obtained by Rowell and Phillips in nmr experiments on PAA.[23] They obtained values of S_{aa}, the average orientation matrix element of the PAA molecules referred to the long molecular axis a, for temperatures between 113 and 134°.

In Figure 6 values of S_{aa} at various temperatures are compared for PAA (as obtained from nmr measurements) and for our elongated radicals dissolved in PAA (as obtained from esr measurements).

The orientation of the solute radicals is always less than that of PAA and is larger for more elongated molecules ($n = 2, 3$). Radicals I and VI have the same order of magnitude for S_{aa}, suggesting a major role played by the number of phenyl rings in determining "orientability."

In Figure 7 values of S_{aa} are reported for the same solutes in PBB. Here nmr data for the pure solvent are lacking, but the fact that solute orientation in the nematic phase of PBB is larger than in PAA suggests that orientation of the solvent is also larger.

An apparent anomaly is found in PBB for radical V whose orientation is larger than that of I and VI. This may be an indication of specific interactions between V and PBB. This idea is supported by observations of Rowell and coworkers[23] that indicate large orientation of benzoic acid in p-hexyloxybenzoic acid. An interaction analogous to the formation of carboxylic acid dimers



would make the orientation of V more closely approach that of the solvent molecules.

Figure 5 also shows the sudden decrease of S_{aa} below 150° to small negative values. It is possible that this is due to a transition of the solvent from a nematic to a smectic phase. The existence of such phases in higher p-alkyloxybenzoic acids has been established,[24] although it was not observed for the butyl case. The direct microscopic observation of such transitions is, however, quite difficult, and it is certain that magnetic resonance is a more sensitive method of detection. Our observations, for example, put the nematic isotropic transition for p-butyloxybenzoic acid very close to 165°. The reported value from direct observation is about 5° lower.[24]

Acknowledgment. We thank Dr. P. L. Nordio for many helpful discussions and for some of the measurements.

(23) J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).

(24) G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).

A Frequency Shift–Enthalpy Correlation for a Given Donor with Various Hydrogen-Bonding Acids

Russell S. Drago, Nelson O'Bryan, and Glenn C. Vogel

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received October 13, 1969*

Abstract: The determination and estimation of enthalpies of adduct formation for t-butyl alcohol with various donors enabled us to incorporate this hydrogen-bonding acid into a linear enthalpy–frequency shift correlation. The wide variation in acidity offered by 1,1,1,3,3,3-hexafluoro-2-propanol, substituted phenols, and butanol provides preliminary evidence for the existence of a linear frequency shift–enthalpy correlation for a given base with various alcohols. These constant-base plots have essentially zero intercept, but the constant-acid plots do not. A theoretical model for the bonding is proposed which is consistent with this observation. The existence of constant-acid and constant-base linear frequency–enthalpy correlations for a series of donors and acceptors requires that a plot of $\Delta\nu_{\mathrm{OH}}$ for phenol *vs.* $\Delta\nu_{\mathrm{OH}}$ for another acid with the same set of bases be linear with zero intercept. The slope of this $\Delta\nu_{\mathrm{OH}}$ *vs.* $\Delta\nu_{\mathrm{OH}}$ line is related to the ratio of the intercepts of this acid and phenol for the constant-acid plots.

Previous articles from this laboratory have dealt with the quantitative evaluation of thermodynamic data for the hydrogen bonding of phenol and various substituted phenols to a series of Lewis bases. Correlations of proton chemical shifts[1] or infrared frequency shifts[2-4] and enthalpies have been sought. A linear relationship between the shift in the frequency of the O–H stretching vibration of phenol, $\Delta\nu_{\mathrm{O-H}}$, and the

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