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points follow very closely the equation given by Hylleraas,¹⁵ except in the region below Z=0.95; our E/Z^2 curve turns fairly sharply and 16 becomes -0.5 a.u.

at Z=0.91, whereas his curve goes up to a maximum and eventually diverges to $-\infty$.

A description of the numerical procedures used in this work for the solution of the variational problem can be found in Refs. 4, and 17.

¹⁷ A. Wallis, D. L. S. McElwain, and H. O. Pritchard, Intern. J. Quantum Chem. (to be published).

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ESR of Spin-Labeled Nematogenlike Probes Dissolved in Nematic Liquid Crystals*

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We show that qualitative information on molecular ordering in nematic mesophases is conveniently obtained from the ESR spectra of trace quantities of spin-labeled rodlike probe molecules dissolved in the nematogen. The synthesis of the probe [2,2,6,6-tetramethyl-4-(p-octyloxy)-benzoylamino-piperidine-1oxyl] is described and ESR spectra of the probe taken in nine solvents at various temperatures are reported. Large contractions of the ¹⁴N hyperfine patterns, as well as positive g shifts, have been observed. This indicates that the alignment of the host molecules along the magnetic field direction constrains the motion of the probe molecules so that they too are aligned parallel to the field. The rotation of the radical group about the bond connecting it to the rest of the probe molecule is partly hindered. In general, the probe molecules described here are less ordered than the host molecules.

I. INTRODUCTION

Nematic mesophases1 are known to assume a macroordered structure in strong magnetic fields, and it is commonly agreed that in this state the long axes of the molecules tend to align with the field.² (Magnetic ordering is apolar and should be described as alignment rather than orientation.) Deviations from complete alignment in strong magnetic fields thus reflect the incomplete extent of micro-ordering which is commonly specified by the parameter S^{2-10} S is measured

³ A. Saupe, Angew. Chem. Intern. Ed. Engl. 7, 97 (1968).
⁴ V. N. Tsvetkov, Acta Physicochim. URSS 16, 132 (1942).

⁶ P. L. Jain, H. A. Moses, J. C. Lee, and R. D. Spence, Phys. Rev. 92, 844 (1953).

by means of any second-rank tensor property of the molecule,⁶ provided the tensor elements are known from an independent measurement in an ordered phase such as a single crystal.

The correct procedure for measuring S is by studying tensor properties pertaining to pure solvent molecules,^{2,6} e.g., nuclear quadrupole interactions of deuterons in deuterated nematogens.² In the present paper we describe an attempt to determine S by observing the ESR of a small quantity of spin-labeled^{11,8} probe molecules dissolved in the diamagnetic host. (Results similar to ours have been obtained by Falle et al.⁸ from the ESR of nitroxide biradicals in liquid crystals.)

Our probe molecules resemble the host molecules in many respects, i.e., they are long, linear, and rather stiff. The probe prepared by us (Fig. 1, IV) only approximates an ideal probe because by itself it does not form a nematic mesophase and as a consequence is always less ordered than the host.

If one of the principal axes of the tensor interactions of the radical is made coincident with the major axis of the probe molecule, the interpretation of the spectra is simplified. In the probe described here the N-O bond direction (x=1 axis) departs from the molecular axis by $\Phi \simeq 10^{\circ}$. This angle is rather invariant to low-barrier deformations of the probe.

¹⁵ E. A. Hylleraas and J. Midtdal, Phys. Rev. 103, 829 (1956). ¹⁶ See also C. W. Scherr, F. C. Sanders, and R. E. Knight, in Perturbation Theory and its Applications in Quantum Mechanics, C. H. Wilcox, Ed. (John Wiley & Sons, Inc., New York, 1966), p. 97.

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¹G. W. Gray, Molecular Structure and the Properties of Liquid

Crystals (Academic Press Inc., London, 1962). ² J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, J. Chem. Phys. **43**, 3442 (1965).

⁶ A. Saupe and W. Maier, Z. Naturforsch. 16a, 816 (1961).

⁷ W. Maier and G. Englert, Ber. Bunsenges Physik. Chem. 64, 689 (1960)

⁸ H. R. Falle, G. R. Lockhurst, H. Lemaire, Y. Marechal, A. Rassat, and P. Rey, Mol. Phys. 11, 49 (1966). ⁹ G. R. Lockhurst, Mol. Cryst. 2, 363 (1967).

¹⁰ A. Saupe, G. Englert, and A. Povh, Advan. Chem. Ser. 63, 51 (1967).

¹¹ A. D. Buckingham and K. A. McLauchlan, in Progress in High Resolution NMR Spectroscopy, J. W. Emsley, J. Feeney, and L. H. Sutcliff, Eds. (Pergamon Press, Ltd., London, 1967), Vol. 2.



FIG. 1. The synthesis of the probe molecule (IV). p-Octyl-oxybenzoic acid (I) is one-half of a nematogen, because its stable carboxylic dimers form a nematic mesophase. (I) Bonds with (II) to form (III), which is then oxidized into (IV). (IV) is a linear molecule in which the N-O bond direction is $\sim 10^{\circ}$ off the major molecular axis. (IV) would not form a nematic phase by itself, and its alignment inside a nematogen is less complete than that of the host molecules.

II. METHOD OF CALCULATION

The spin Hamiltonian describing the ESR of a nitroxide radical in a nematic solvent is⁹ (Appendix)

$$\mathcal{K} = (g + \Delta g)\beta H_0 S_z + h(A + \Delta A) I_z S_z, \qquad (1)$$

where g and A are the isotropic invariants of the gtensor and of the hyperfine tensor of the electron with the ¹⁴N nucleus, respectively, and the deviations from isotropy are

$$\Delta g = \frac{1}{3} (2g_{xx} - g_{yy} - g_{zz}) S_{11} + \frac{1}{3} (g_{zz} - g_{yy}) (S_{33} - S_{22})$$

= 0.0030S_{11} - 0.0011 (S_{33} - S_{22}), (2)

$$\Delta A = \frac{2}{3} (A_{zz} - A_{\perp}) S_{33}; \quad \Delta A \text{ (in gauss)} \sim 17.3 S_{33}. \quad (3)$$

The frame of reference is the one in which both g and A tensors are diagonal.^{12,13} All four CNOC atoms are considered coplanar; the z axis is perpendicular to the plane, x and y are in the plane, and the x axis is extended along the N-O bond (Fig. 1).

In this frame the g and the A tensors have the following elements¹²: $g_{xx} = 2.0089$; $g_{yy} = 2.0061$; $g_{zz} = 2.0027$; $g = \frac{1}{3} \sum_{x} g_{ii} = 2.0060$. $A_{zz} = 32$ G; $A_{xx} = A_{yy} = A_{\perp} = 6$ G; $A = \frac{1}{3} \sum_{x} A_{ii} = 15$ G. The values are pracically equal for the methyl-protected nitroxide radi cals,¹² and we have used them to derive the numerical coefficients in Eqs. (2) and (3).

The "distortion theory" ordering parameters S_{ii} ^{9,10,13} measure deviations (+ or -) from isotropy in the probability of having the *i*th axis of the radical aligned along the magnetic field. $S_{ii} = +1$ when $H_0 \parallel X_i$, $S_{ii} =$

Phys. 43, 2909 (1965).

 $-\frac{1}{2}$ when $H_0 \perp X_i$ and $\sum S_{ii} = 0$. The operational definitions of Δg and ΔA are given in Fig. 4. If the probe molecules align as expected, then ΔA and S_{33} are both negative.

The number of independent S_{ii} parameters is reduced from two to one if the radical group rotates about its x axis relative to the rest of the probe molecule. In this case the $y \equiv 2$ and $z \equiv 3$ axes have equal probabilities of being perpendicular to H_0 and one gets $-S_{22} = -S_{33} = \frac{1}{2}S_{11}$.¹⁰ Then Eqs. (2) and (3) reduce to

$$\Delta A \text{ (in gauss)} = -8.6 \times S_{11}; \quad \Delta g = 0.0030 \times S_{11}. \quad (4)$$

The validity of Eq. (4) may be verified graphically (Fig. 3). In the Δg , ΔA plane (properly normalized) each spectrum is represented by a point. The locus of the points would be the diagonal of unity slope if Eq. (4) is satisfied. Departures from unity slope would indicate the inequality of S_{22} and S_{33} .

III. MATERIALS

A. The Synthesis of the Probe Molecule

The probe molecule (Fig. 1, IV), 2,2,6,6-tetramethyl-4-(p-octyloxy)-benzoylamino-piperidine-1-oxyl-(IV), was prepared by the oxidation of 2,2,6,6-tetramethyl-4-(p-octyloxy)-benzoylamino-piperidine(III), which in its turn was obtained by coupling p-octyloxybenzoic acid(I) to 2,2,6,6-tetramethyl-4-aminopiperidine (II) (Fig. 1).

A solution of 5 g of (I), 3.12 g of (II), and 5 g of



FIG. 2. Typical ESR spectra of the probe radical IV dissolved in isotropic (140°-top) and nematic (85°-bottom) 4,4-hexyl-oxyazoxybenzene (PAHB-Table I, No. 5). In all the spectra observed the external hyperfine components were equidistant from the middle component.

¹² C. L. Hamilton and H. M. McConnell, in *Structural Chemistry* and *Molecular Biology*, A. Rich and N. Davidson, Eds. (W. H Freeman and Co., San Francisco, Calif., 1968), p. 115. ¹³ O. H. Griffith, D. W. Cornell, and H. M. McConnell, J. Chem.

T(°C)	$-\Delta A$ (G)	$\Delta g \times 10^3$	Sn	S ₂₂	S ₈₃	T(°C)	$-\Delta A$ (G)	$\Delta g imes 10^3$	<i>S</i> 11	S ₂₂	S33
1. CH ₃ OC ₆ H ₄ N:NOC ₆ H ₄ OCH ₃ ;						110	3.0	1.24	0.47	-0.30	-0.17
4,4'-Azoxy dianisole = PAA (9723;710)						100	3.5	1.42	0.53	-0.33	-0.20
135 ср				A 40	0.44	90	4.0	1.67	0.68	-0.40	-0.23
130	2.25	0.87	0.31	-0.18	-0.13	85	4.1	1.79	0.69	-0.48	-0.24
120	2.75	1.05	0.38	-0.22	-0.16	81	4.3	1.98	0.78	-0.53	-0.25
117 mp						80 mp					
110	3.00	1.11	0,40	-0.23	-0.17		CHC		NCHO	сч.	
100	3.25	1.30	0.48	-0.29	-0.19	p-phenetyl-azophenyl hexanoate (922 102; ···)					
2. $CH_3OC_6H_4CH: NC_6H_4N: NC_6H_5;$ <i>N-p</i> -methoxybenzylidene- <i>p</i> -phenylazoaniline (8545; 675)						118 ср					
190 ср						110	1.75	0.46	0.13	-0.03	-0.10
185	1.4	0.46	0.15	-0.07	-0.08	100	2.35	0.77	0.25	-0.11	-0.14
180	1.65	0.56	0.20	-0.11	-0.09	90	2.75	0.93	0.32	-0.15	-0.16
175	1.9	0.74	0.27	-0.16	-0.11	80	3.00	1.00	0.34	-0.17	-0.17
170	2.0	0.74	0.28	-0.16	-0.12	70 mp	3.35	1.05	0.34	-0.15	-0.19
160	2.3	0.86	0.31	-0.18	-0.13	60	3.75	1.11	0.34	-0.12	-0.22
150	2.65	1.00	0.36	-0.21	-0.15	55	4.00	1.24	0.39	0.16	-0.23
148 mp											
140	2.65	1.11	0.43	-0.28	-0.15	7. CH_2 : CH (CH ₂) ₈ COOC ₆ H ₄ N: NC ₆ H ₄ OC ₂ H ₅ ; 4-(<i>p</i> -ethoxyphenylazo)-phenyl-10-undecanoate (922 353; ···)					
130	2.9	1.17	0.43	-0.26	-0.17	105 ср					
3. CH ₃ OC ₆ H ₄ CH:NN:CHC ₆ H ₄ OCH ₃ ;						100	2.5	0.93	0.34	-0.20	-0.14
189 ср	P	-Allisalazi	lie (0340)	,		90	3.0	1.17	0.43	-0.26	0,17
185	1.5	0.46	0.14	-0.05	-0.09	80	3.5	1.39	0.52	-0.32	-0.20
180	1.9	0.74	0.27	-0.16	-0.11	70	3.75	1.55	0.58	0.36	-0.22
175 mp						60 mp	4.1	1.67	0.62	-0.38	-0.24
170	2.4	1.00	0.38	-0.24	-0.14					nacia coid	
165	2.65	1.05	0.39	0.24	-0.15	8, C8H17	Cariro Carico Con; p-OctyloxyDelizoic aciu				
160	2.8	1.05	0.38	-0.22	-0.16	150 cp					
4. CH ₂ OC ₆ H ₄ CH:NC ₆ H ₄ CH:CHCOOC ₂ H ₅ ; Ethyl- <i>p</i> -[(<i>p</i> -methoxybenzylidene)amino]-cinnamate (10 306; ···)						140	1.9	0.80	0.30	0.19	-0.11
						130	2.5	1.00	0.38	-0.24	-0.14
141 ср		· ·				120	2.9	1.24	0.47	-0.30	-0.17
140	1.25	0.37	0.12	-0.05	-0.07	110 mp	3.5	1.36	0,50	-0.30	-0.20
135	1.50	0.62	0.23	-0.14	-0.09	9. Low-ten	nperature	mixture 1	:1:1 wei	ght ratio of	Refs. 5-7
130	1.75	0.68	0.25	-0.15	-0.10	130 cp					
120	2.0	0.74	0.26	-0.14	-0.12	120	2.5	0.93	0.33	-0.20	-0.14
108 mp						100	3 1	1 24	0.46	-0.28	-0.18
5. $C_6H_{10}OC_6H_4N: NOC_6H_6OC_6H_{18};$ 4. 4' herviory a zoryhenzene = PAHR (10, 120, 648)						80	3.75	1,55	0.58	-0.36	-0.22
τ_{1} $\tau_{-\mu}$ τ_{2} $\tau_{$						60	4,25	1.85	0.71	-0.46	-0.25
120	2.25	0.93	0.35	-0.22	-0.13	40	4.8	2.04	0.77	-0.49	-0.28
120	4.43	0.75	0.00	-0.22	-0.10	1	4.0	2.01	0.11	0.1/	0.40

TABLE I. The measured temperature dependence of ΔA and Δg and of the ordering parameters S_{ii} of the ESR spectra of radical IV dissolved in nine different nematic solvents.^a

^a The name and formula of each of the solvents and the catalog numbers of the products as marketed by Eastman Organic Chemicals or by Frinton Laboratories are given sequentially in parentheses. The measurements were made as the temperatures were sequentially lowered, so that the nematic mesophases supercooled. cp is the clearing point (temperature of nematic-isotropic transition) and mp is the melting point (solid-nematic transition temperature).



FIG. 3. A plot of the (properly normalized) measured hyperfine decrements (ΔA) versus the g shifts (Δg) of the ESR spectra of molecule IV in PAHB (Table I, No. 5) and in p-phenetylazophenyl-hexanoate (Table I, No. 6). The normalizing coefficients are chosen so that the diagonal of unity slope would agree with formula (4) and give S_{11} directly. Equation (4) is roughly obeyed for the solvents of Table I, because the points depicted here are those of greatest deviation from the diagonal.

1-ethyl-3-(3'-N,N-dimethylaminopropyl) carbodi-imide hydrochloride¹⁴ in 50 ml CHCl₃ was stirred 2 h at ice temperature and then 3 h at room temperature. The solution is then diluted with 150 ml of CHCl₃, washed with 6% aqueous sodium chloride solution and with 6% aqueous sodium bicarbonate solution and dried over anhydrous sodium sulfate. Following filtration which removed the drying agent, the filtrate was concentrated *in vacuo* to give 6 g (77%) of (III), which may be recrystallized from *n*-hexane, mp. 87°–88°C.

Analysis: Found: C, 73.92%; H, 10.23%; N, 7.09%. $(C_{24}H_{40}N_2O_2 \text{ contains } C, 74.18\%; H, 10.36\%; N, 7.21\%).$

The structure of (III) was confirmed by mass spectrometry.

Two and one-half grams of (III) were suspended in 200 ml of a mixture of methyl alcohol and water (volume ratio 4:1), to which 0.35 g of sodium tungstate, 0.3 g of EDTA, and 5 ml of 30% aqueous hydrogen peroxide¹⁵ were added. The reaction mixture was stirred 24 h at room temperature and then filtered. The yellow solid was suspended and stirred in 100 ml of aqueous HCl, 1N, filtered and washed with water, with diluted aqueous NaOH, and with water again. After drying *in vacuo*, the yield of (IV) was 1 g (38%). The product may be recrystallized from *n*-hexane, mp. 88°C.

Analysis: Found: C, 72.06%; H, 9.94%; N, 6.84%. $(C_{24}H_{39}N_2O_3 \text{ contains } C, 71.43\%; H, 9.74\%; N, 6.94\%).$

The structure of (IV) was confirmed by mass spectrometry.

B. Nematic Solvents

The solvents we used are listed in Table I. They were purchased from Eastman Organic Chemicals, Rochester 3, New York, and from Frinton Laboratories, P.O. Box 301, Grant Avenue, South Vineland, New Jersey 08360, and the respective catalog numbers are given in Table I.

The powders were contaminated with the probe and sealed in Pyrex tubes after several freeze-pump-thaw cycles.

IV. RESULTS AND DISCUSSION

Electron spin resonance spectra of each sample were taken in a sequence of descending temperatures. The spectrometer was a Varian E-3 (9.15 MHz) equipped with the Varian temperature controller. The nematic phases of all the samples persisted well into the supercooled state.

Spectra of the probe (Fig. 1, IV) in isotropic (140°C) and in nematic (85°C) 4,4'-hexyloxyazoxybenzene (PAHB) (Table I, No. 5) are shown in Fig. 2. The anticipated changes in the spectra are evident.

The values of Δg and ΔA given in Table I were derived from all the spectra by the criteria given in Fig. 4.

The S_{ii} parameters pertaining to all the spectra



FIG. 4. Graphical presentation of the ESR spectra of molecule(IV) (Fig. 1) dissolved in isotropic (top), nematic (middle), and oriented single-crystal¹² (bottom) phases. Operational definitions of A, ΔA , g, and Δg are sketched. The x=1 axis coincides with the N-O bond direction in the radical and the $x \mid \mid H_0$ spectrum is the limiting case in which the x axes of all the radicals are parallel to H_0 . The ESR spectrum in the nematic phase is a linear interpolation between the isotropic spectrum and the spectrum in which the x axes of all the radicals are aligned parallel to H_0 . The assumption of rotational symmetry about the x axes of the probe molecules is implicit in this presentation.

 ¹⁴ F. Kurzer and K. Douragi-Zadeh, Chem. Rev. 67, 107 (1966).
¹⁵ E. G. Rozentzev and L. A. Krinitzkaya, Tetrahedron 21, 491 (1965).





FIG. 5. The temperature dependence of the ordering parameters derived from the ESR of the probe. (a) S_{ii} parameters of the probe in PAA (Table I, No. 1). The ordering parameter of the pure solvent^{3,6,7} is shown. This case is representative of the majority of solvents studied. Typically $S_{11} < S$. (b) S_{ii} parameters of the probe in *p*-phenetyl-azophenyl hexanoate (Table I, No. 6). In this solvent $|S_{33}| > |S_{22}|$ while in all the other solvents the opposite inequality obtains. (c) S_{ii} parameters of the probe in PAHB (Table I, No. 5), with the ordering parameter of the solvent also included.⁷ This system is exceptional in the large value of S_{11} and in the large difference $|S_{22}| - |S_{33}|$ at lower temperatures.

(Table I) were derived from the measured $\Delta g - \Delta A$ pairs of numbers by means of Eqs. (2) and (3) and the traceless property of the ordering parameters.

Equation (4) is approximately obeyed by all the samples. Data for two samples, PAHB (Table I, No. 5) and p-phenetyl-azophenyl hexanoate (Table I, No. 6) which show the largest deviations from agreement with Eq. (4) are plotted in Fig. 3. We thus conclude that the probe molecule can be approximated by an axially symmetrical rod whose alignment is characterized by a single parameter, e.g., S_{11} . The assumption of axial symmetry about the x axis is implicit in Fig. 4, where the ESR spectrum in the "nematic" region is a linear interpolation between the isotropic spectrum and the spectrum of molecules fully aligned along one axis.

The deviations from axial symmetry are of some interest. The negative values of S_{22} and S_{33} indicate that the $y \equiv 2$ and $z \equiv 3$ axes of the radical tend to be

perpendicular to H_0 (they would be fully perpendicular when $S_{22}=S_{33}=-\frac{1}{2}$). Now in *p*-phenetyl-azophenyl hexanoate (Table I, No. 6), Figs. 3 and 5(b), $|S_{22}| < |S_{33}|$, $|S_{33}|$, whereas in all the other solvents $|S_{22}| > |S_{33}|$. The solvent PAHB (Table I, No. 5), Figs. 3 and 5(c), is singled out by the large values of S_{11} and $|S_{22}| - |S_{33}|$ at lower temperatures.

One possible way of visualizing the inequality of S_{22} and S_{33} is sketched in Fig. 6. We have no explanation for this behavior. The S values for the pure solvent molecules have been measured by various authors.²⁻¹⁰ These values are compared with our S_{11} data in Figs. 5(a) and 5(c) and obviously $S_{11} < S$.

Interesting qualitative information has been obtained on trends of ordering in supercooled nematic solvents. Without exception the ESR spectra indicate that solvent ordering further increases in the supercooled nematic phase.



 $s_{22}, s_{33} < 0 < s_{11}; 1 s_{22} > 1 s_{33}$



 $s_{22}, s_{33} < 0 < s_{11}; 1 s_{22} < 1 s_{33}$

FIG. 6. Representation of the motion of the radical probe molecule in two different nematic solvents for the cases in which $|S_{22}| > |S_{33}|$ and $|S_{22}| < |S_{33}|$, respe. ctively

The low-temperature mixture (Table I, No. 9) must be preheated to $\sim 100^{\circ}$ C and then can be maintained as a supercooled nematic phase at any temperature above 45°C.

V. CONCLUSIONS

(1) The ESR of nitroxide radicals is a convenient and straightforward source of information on molecular ordering in nematic mesophases.

(2) The probe molecule described here is a very good approximation of a spin-labeled nematogen. Further synthetic work which would emphasize the nematic properties of the probe molecules is desirable.

APPENDIX

The spin Hamiltonian for the nitroxide radical is

$$\mathfrak{K} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + h \mathbf{I} \cdot A \cdot \mathbf{S}, \tag{5}$$

where I is the nuclear spin operator and A is the hyperfine coupling tensor with the ¹⁴N nucleus. In the high field approximation Eq. (5) reduces to

$$\mathcal{K} = \beta H_0 g_{ZZ} S_Z + h A_{ZZ} I_Z S_Z$$

+[
$$\beta H_0(g_{ZX}S_X+g_{ZY}S_Y)+hI_Z(A_{ZX}S_X+A_{ZY}S_Y)$$
]. (6)

 g_{ZZ} and A_{ZZ} are then expressed in terms of the tensor components in the special molecular frame xyz (Figs. 1 and 6) in which both the g and the A tensors happen to be diagonal.¹² $\cos(Z, x_i)$ is the direction cosine between the molecular x_i axis and the field H_0 ,

$$g_{ZZ} = g_{xx} \cos^2(Z, x) + g_{yy} \cos^2(Z, y) + g_{zz} \cos^2(Z, z)$$

= $\frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) + \frac{2}{3} \{\frac{1}{2} [3 \cos^2(Z, x) - 1] g_{xx} + \cdots \}.$
(7)

Equation (7) and the analogous expression for A_{ZZ} are inserted in Eq. (6). The nematic liquid-crystalline ordering in the magnetic field is characterized by the random rotational motion of the molecules (or their clusters) about the Z axis at rates which are fast in comparison with the precessional frequency. The time averages of the bracketed terms in Eq. (6) vanish because the field H_0 may give rise to a transverse component of **S** as well as to its negative, whereby $\langle g_{ZX} \rangle = \langle g_{ZY} \rangle = \langle A_{ZX} \rangle = \langle A_{ZY} \rangle = 0$. The time averages of the brackets of Eq. (7) are defined as $\langle \frac{1}{2} [3 \cos^2(Z, x) - 1] \rangle = S_{11}, \cdots$, and obviously $\sum S_{ii} = 0$ because the corresponding unaveraged sum vanishes at any instant. The time average of Eq. (6) is then

$$\mathcal{K} = \beta H_0(g + \Delta g) S_Z + h(A + \Delta A) I_Z S_Z, \tag{8}$$

$$g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}); \quad A = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz}), \quad (9)$$

and

$$\Delta g = \frac{2}{3} (S_{11}g_{xx} + S_{22}g_{yy} + S_{33}g_{zz}), \qquad (10)$$

$$\Delta A = \frac{2}{3} \left(S_{11} A_{zz} + S_{22} A_{yy} + S_{33} A_{zz} \right). \tag{11}$$

Because of the zero-trace property of S_{ii} and the equality of $A_{xx} = A_{yy} = A_{\perp}$ in the nitroxide radical,¹² Eqs. (10)-(11) reduce to Eqs. (2) and (3), respectively.