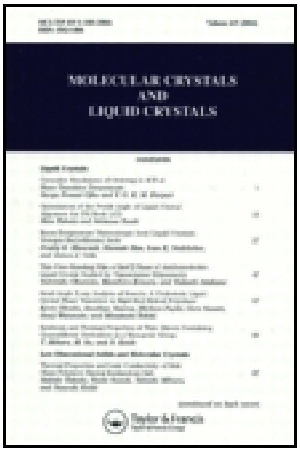

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# Orientation of Small Molecules in a Nematic Liquid Crystal as Studied by Electron Spin Resonance

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# Orientation of Small Molecules in a Nematic Liquid Crystal as Studied by Electron Spin Resonance

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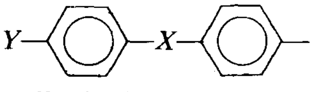
Based on the measurements of hyperfine splitting constants (*hfsc*) of small aminoxyl (nitroxide) radicals in the nematic phase of *N*-4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) we discussed the relation between the molecular orientation and the molecular shapes, especially the contribution of the phenyl groups to the molecular alignments.

## INTRODUCTION

In the nematic phase the solvent molecules and also radical probes align their long axes along the magnetic field. The molecular arrangement of radicals in the nematic solvents have been studied extensively by ESR.[1-3] When the radical probes are large and prolate or oblate molecules, such as cholestane, spin-labeled fatty acid, and vanadyl complexes etc., they have good alignment because of their length or flatness. However even for the small and spherical radicals weak alignment has also been observed. The small and spherical radicals in this report are about 10 Å in the longest diameter and their ratios of the length of long axes to those of other two axes are smaller than 1.67.

Most of the molecular structure of materials which have the liquid crystalline mesophases are  and the benzene rings are thought to be effective in forming the liquid crystalline mesophases because of their contribution to the molecular polarity and linearity. Therefore in the present study we examined the alignments of the small and spherical spin probes by choosing various molecular shapes and also by changing the substituent to elucidate the factor which rules the molecular alignment.

## EXPERIMENTAL

The aminoxyl spin probes used are shown in Figure 1.

(1) Di-*t*-butylaminoxyl (DTBN)
(2) 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)
(3) 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL)
(4) 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (TEMPONE)
(5) Di-phenylaminoxyl (DPNO)
(6) *N*-*t*-butylphenylaminoxyl
(7) *N*-ethylphenylaminoxyl
(8) Phenyl adduct of α-phenyl-*N*-*t*-butylnitrone (PBN)

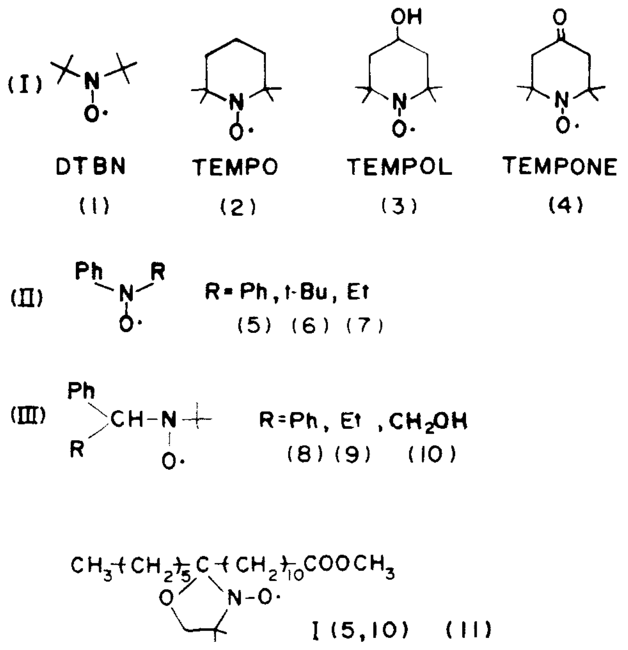


FIGURE 1 The structure of aminoxyl radicals.

(9) Ethyl adduct of PBN
(10) Methanol adduct of PBN
(11) 2-(10-carboxyldecyl)-2-hexyl-4,4-dimethyl-3-oxazolidinyloxyl methyl ester (I(5,10))

DTBN (1) was purchased from Eastman Kodak Co. and was used without further purification. TEMPO (2), TEMPOL (3), and TEMPONE (4) were synthesized by the methods shown in the literature.[4] DPNO (5), (6), and (7) were synthesized through the reactions of Grignard reagents with corresponding nitroso compounds. (8) and (9) were produced through the reactions of PBN with Grignard reagents. (10) was produced through the abstraction of a proton from methanol by photoexcited benzophenone (BP) followed by spin trapping with PBN. I(5,10) (11) were purchased from Aldrich Chemical Co. It was used without further purification.

The nematic liquid crystal *N*-(4-methoxybenzylidene)-4′-*n*-butylaniline (MBBA) purchased from Tokyo Kasei Co. was recrystallized from ethanol and then molecular-distilled. Its purity was 99.5% as found by differential scanning calorimetry (DSC). The $10^{-3}$ M solution of aminoxyl radical was packed in 4 mm i.d. cylindrical sample tubes and they were degassed by the usual freeze-thaw technique on a vacuum line and were sealed off under vacuum. The concentration was sufficiently low to avoid exchange broadening of spectra. Transition temperatures of the liquid crystal solutions were found to be lowered by 2–3°C by the addition of the spin probes. The *hfsc* and $g$ values at the temperature by 13°C lower than $T_c$ were chosen as values in the nematic phase for the calculation of the order parameter. ESR spectra were measured by a home-made $X$-band spectrometer with a JOEL 30 cm magnet under 200 Hz field modulation of small amplitude and the accuracy in the determination of *hfsc* was ±0.001 mT.

## RESULTS AND DISCUSSION

In a nematic phase the elements of ordering matrix $S_{ij}$ are defined by $S_{ij} = \langle 3l_il_j - \delta_{ij}\rangle/2$ where $l_i$ is the direction cosine between the molecular axis and the direction of the magnetic field.[5] The partial alignment of a radical causes shifts in the observed hyperfine splitting and $g$ values. They are given by

$$\Delta A = S_{33}A'_{zz} + (S_{11} - S_{22})(A'_{xx} - A'_{yy})/3 \tag{1}$$

$$\Delta g = S_{33}g'_{zz} + (S_{11} - S_{22})(g'_{xx} - g'_{yy})/3 \tag{2}$$

TABLE I

Observed *hfsc* shift, $S_{33}$, and $S_{mol}$

| Groups | Radicals | $\Delta A_N$/mT | $S_{33}$ | $\xi$ | $S_{mol}$ |
|---|---|---|---|---|---|
| (I) | (1) | −0.050 | −0.030 | 90° | +0.060 |
| | (2) | −0.073 | −0.044 | 90° | +0.088 |
| | (3) | −0.059 | −0.035 | 90° | +0.070 |
| | (4) | −0.122 | −0.073 | 90° | +0.146 |
| (II) | (5) | −0.25 | −0.15 | 90° | +0.30 |
| | (6) | −0.17 | −0.10 | 90° | +0.20 |
| | (7) | −0.13 | −0.078 | 90° | +0.16 |
| (III) | (8) | +0.176 | +0.11 | 20° | +0.13 |
| | (9) | +0.164 | +0.098 | 20° | +0.12 |
| | (10) | +0.074 | +0.044 | 30° | +0.070 |
| | (11) | +0.355 | +0.19 | 0° | +0.19 |

where $A'_{ii}$ and $g'_{ii}$ are the elements of the traceless anisotropic hyperfine and $g$ tensors.[6] If the molecules possess cylindrical symmetry, Eq. (1) will be reduced to

$$\Delta A = S_{33} A'_{zz} . \qquad (3)$$

Principal values of the hyperfine and $g$ tensors are not known for all the radicals studied here, however, when $A'_{zz}$ are calculated for six stable aminoxyl radicals whose principal values have been known, they are ranged within 1.67–1.84 mT.[7] Therefore we adopted the principal values of DTBN[7] as a typical example of aminoxyl radicals studied here, then the order parameter $S_{33}$ calculated by Eq. (3) are reliable with the accuracy of ±0.007. (Here we used the results in Table I).

TABLE II

Observed shifts of ESR parameters and order parameter

| Radicals | $\Delta A_N$/mT | $\Delta g$ | $S_{33}$ (a) | $S_{33}$ (b) |
|---|---|---|---|---|
| DTBN | −0.050 | $-1 * 10^{-4}$ | −0.030 | −0.024 |
| Phenyl adduct | +0.176 | $-4 * 10^{-4}$ | +0.106 | +0.108 |

[a] Under cylindrical symmetric condition.
[b] Under asymmetric condition.

Generally the symmetry of aminoxyls are reported to be fair, however, we first checked the adequacy of the approximation. The results for DTBN and phenyl adduct are shown in Table II. As can be seen, the cylindrical symmetry was found to be fair, and the approximation is good for all the other radicals used here. The accuracy of $S_{33}$ are $\pm 0.006$. Therefore total error of $S_{33}$ is $\pm 0.013$.

However calculated $S_{33}$ indicates the direction of the nitrogen $2p\pi$ orbital to the external magnetic field. In general molecular alignment can be discussed by using the order parameter $S_{\text{mol}}$ of the long molecular axis. $S_{\text{mol}}$ can be determined from the experimental $S_{33}$ by the following relation

$$S_{\text{mol}} = S_{33}[\langle 3\cos^2\xi - 1\rangle/2]^{-1} \tag{4}$$

where $\xi$ denotes the angle between the long molecular axis and the NO bond axis.[7] $\xi$ was determined from the molecular geometry and McConnell's relation for β-proton.[8]

For convenience of discussing the molecular alignment, aminoxyl radicals (1)–(10) were classified into three groups (Figure 1). Radicals which belong to the group (I) are all small and spherical. They are about 8 Å in the diameter and their ratios of the largest diameter to those of other two axes are smaller than 1.67. The group (II) are also small but they are oblate and the ratios are about 3.3–2.5. The group (III) are spherical but their molecular sizes are larger than the group (I). (Their diameters are about 10 Å). The spectra of DTBN and phenyl adduct are shown in Figure 2. The *hfsc* shifts and the calculated order parameters $S_{33}$ and $S_{\text{mol}}$ are shown in Table I.

Among the radicals of the group (I) $S_{\text{mol}}$'s are similar except TEMPONE. TEMPONE has a carbonyl group and is more planar than others so it shows better alignment to the direction of the magnetic field resulting in large $S_{\text{mol}}$. In the group (II) two phenyl groups of the radical DPNO are coplanar, which makes the molecule oblate. Therefore it indicates very good alignment and $S_{\text{mol}}$ is larger than that of spin-labeled fatty acid I(5,10) which is long alkyl chain molecule. (See Figure 1 and Table I.) The $S_{\text{mol}}$ of MBBA has been measured by NMR and the value was reported to be 0.53 at the temperature by 13 C lower than the transition temperature.[9] When one phenyl group of DPNO was substituted by a *t*-butyl (6) and an ethyl (7) group, $S_{\text{mol}}$'s become smaller but they are comparable to that of I(5,10). When both phenyl groups were substituted by *t*-butyl groups, DTBN, $S_{\text{mol}}$ becomes smaller than those for (6) and (7). It is reasonable to conclude that phenyl groups dominate the molecular

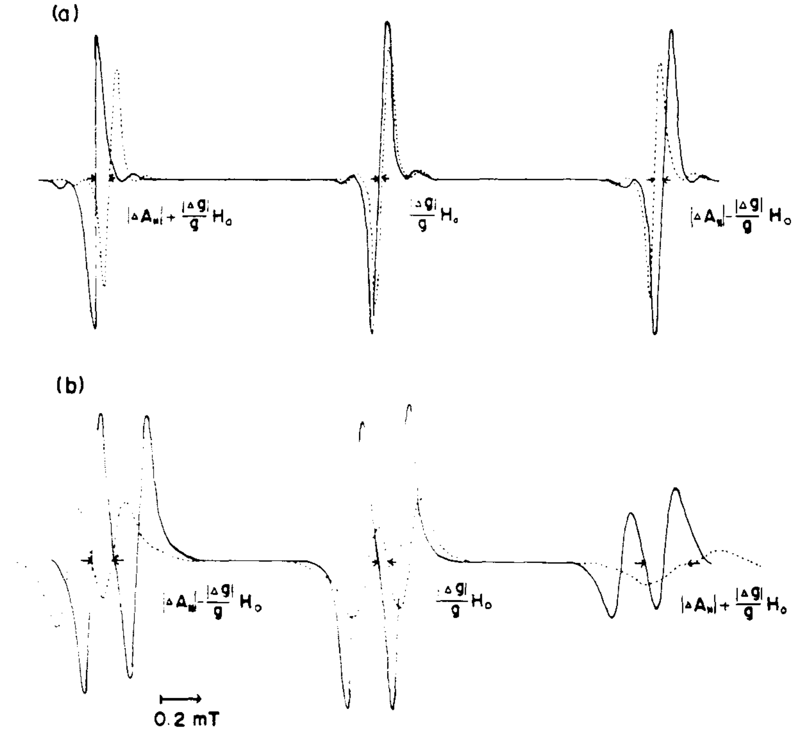


FIGURE 2 ESR spectra of (a) DTBN and (b) phenyl adduct. ——— Isotropic phase; ----- Nematic phase.

alignment because in this case phenyl groups make the molecules oblate. However in the group (III) they have also phenyl groups but their molecular alignments are not as good as those of the group (II). In this case two phenyl groups of radical (8) can not take the coplanar conformation because of the steric hindrance, moreover molecular shapes are spherical. $S_{mol}$ of (10) is much smaller than those of (8) and (9) because in (10) hydrogen bond forms the chelate ring and the ring is nearly perpendicular to the phenyl group.

## CONCLUSIONS

The interesting aspects of the results reported here are 1) even the small molecules indicates the good molecular alignments to the external magnetic field when they are oblate, 2) the effect of phenyl groups on the molecular alignments is remarkable when they are coplanar or they make the molecules oblate, however, if they do not take the coplane, their effect of orienting the molecules is reduced considerably.

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