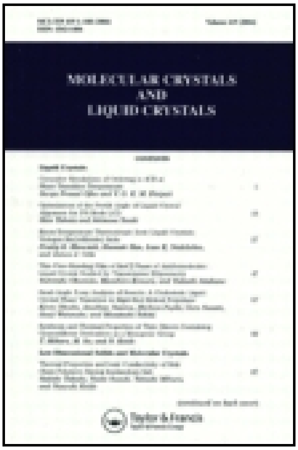

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E.S.R. Investigation of Spin Probes: Not Unique Ordering in Smectic Mesophases

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E.S.R. Investigation of Spin Probes

Not Unique Ordering in Smectic Mesophases

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E.S.R behaviour of various nitroxide probes dissolved in two mesomorphic compounds of the homologous series methoxy-benzylidene-alkyl-cinnamates is investigated. Probe alignment by the mesomorphic host molecules is not unique in smectic phases; intercalation of the probe between the smectic layers occurs, depending on the comparative strength of lateral and inter-layer correlations.

I INTRODUCTION

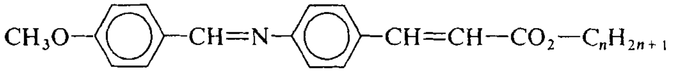
Electron spin resonance (ESR) of solute paramagnetic probes is a convenient technique currently used to investigate macroscopic orientation, microscopic order and rotational motions in liquid crystals.[1] The most commonly used spin probes are long shaped rigid molecules, such as androstane nitroxide derivative, which reflect the local order of the host molecule long axis. We investigate here, the ordering of five nitroxide probes, with various length and flexibility, dissolved in homologous methoxy-benzylidene-amino-alkyl-cinnamates which present nematic, smectic A and smectic B thermotropic mesophases.

The mesomorphic molecules are made up of a rather rigid aromatic core and a flexible alkyl end chain. In a crude picture, we can assume the existence of two kinds of local environment for a spin probe in smectic mesophases: a rather rigid anisotropic environment defined by the interacting rigid cores and a rather fluid one defined by the chains. Depending on the spin probes and on the mesophases, different localizations and different motions can be expected for the nitroxide radicals which will exhibit typical ESR spectra.

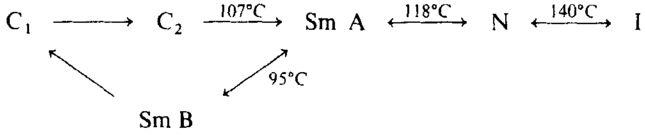
II METHODS

1 Materials

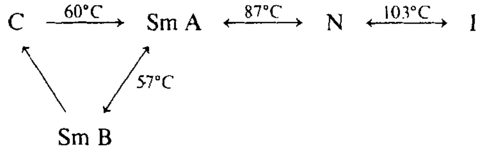
The general formula of methoxy-benzylidene-amino-alkyl-cinnamates is:



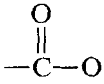
A preliminary study of this series was previously achieved[2] and here we turn our attention to a short chain compound: $n = 2$ (2MBAC) and a longer one: $n = 6$ (6MBAC). 2MBAC was prepared by condensing equimolar quantities of anisaldehyde and ethyl *p*-aminocinnamate in ethanol; then, it was recrystallized three times from a cyclohexane-hexane mixture. 6MBAC was synthetized in the "Laboratoire de Chimie Organique des Hormones" (J. Jacques)†. Both compounds exhibit nematic, smectic A, monotropic supercooled smectic B mesophases. The transition temperatures are measured by optical microscopy:



2MBAC



6MBAC

Smectic B mesophase is uniaxial with long molecular axis normal to the smectic planes as in smectic A. The molecules are asymmetric; due to π bonding, the atoms between the methoxy group and the  $-\overset{\overset{\displaystyle O}{\|}}{C}-O$ group make a rather rigid core; in contrast, the alkyl terminal chain is flexible. The length of the extended molecules measured on molecular models are 22,7 Å for 2MBAC and 27,6 Å for 6MBAC.

The five spin probes are nitroxide derivatives represented in Figure 1. Lengths, molecular frame which diagonalizes hyperfine and g tensors, principal values of these tensors are also reported. There is no isomorphism between these probes and the mesomorphic molecules. Nevertheless, probes I and II, which are long and rigid molecules, are well oriented by the meso-

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† Collège de France, Paris, France.

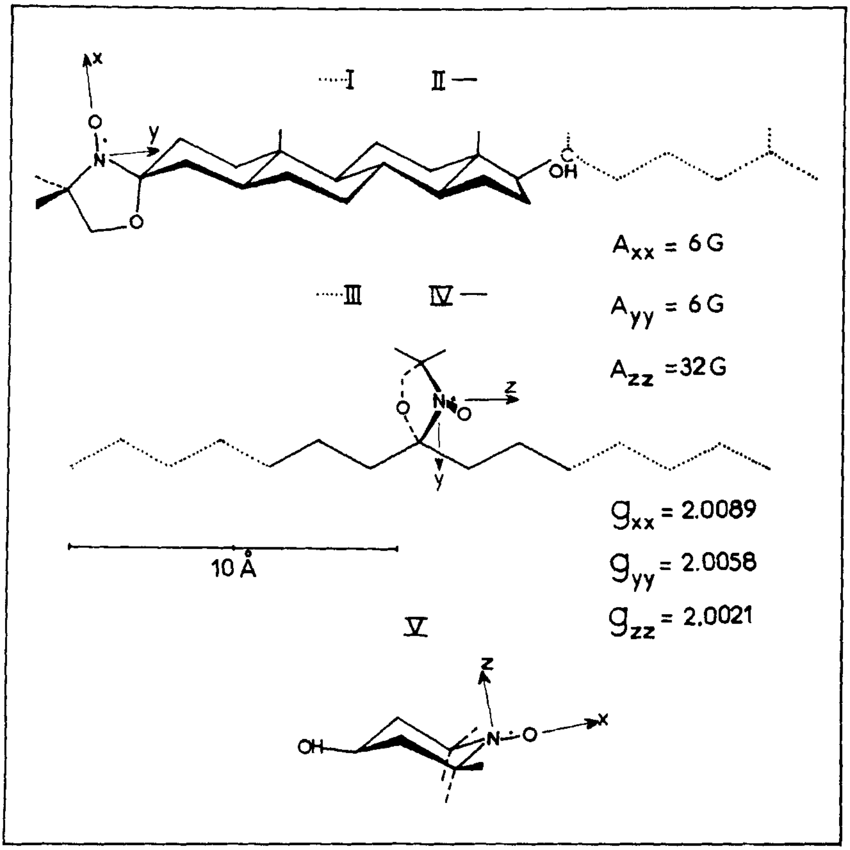


FIGURE 1 Nitroxide spin probes. Probe long axes are horizontal. The principal values of $\hat{g}$ tensor are those of Reference 3; the principal values of $\hat{A}$ were corrected in order to be consistent with the experimental isotropic value of the splitting and the calculated value of maximum order.

morphic solvent and the degree of order of the probe long axis can be expected to be similar to the solvent one. Probes III and IV are highly flexible and intramolecular motions add to global motions lowering the degree of order experienced by the $>N\dot{-}O$ group. Probe V is a rather rigid molecule, disc-shaped, and is expected to be less sensitive to the ordering potential.

2 Experimental

The experiments were performed on a Varian 4502 spectrometer equipped with a variable temperature device. Samples containing nitroxide (10^{-3} M) are prepared between parallel glass plates. Nematic mesophases are oriented by the 3.3 KG working field. Oriented smectic A and B are obtained by setting the samples in a 10 KG field and cycling N ↔ Sm A transition in this field. No reorientation occurs when rotating the smectic samples in the working field. Value of the hyperfine splitting below the N ↔ Sm A transition is used as a test for good orientation: best orientation corresponds to extremum value of this splitting. For powder spectra, the samples were prepared by smashing a prealably labelled amount of the mesomorphic compound; a disoriented smectic sample is obtained by melting the powder between plates.

3 E.S.R spectra analysis

The E.S.R. theoretical basis of paramagnetic probes dissolved in mesophases are now well known. Let us recall some useful relations.[1,4] The spin Hamiltonian, neglecting nuclear Zeeman interaction is:

$$\mathscr{H} = \beta\mathbb{S}\cdot\hat{g}\cdot\mathbb{B} + h\mathbb{S}\cdot\hat{A}\cdot\mathbb{I}$$

where $\mathbb{S}$, $\mathbb{I}$ are the electronic and nuclear spin operators, $\hat{g}$ and $\hat{A}$ the hyperfine tensors, $\mathbb{B}$ the static magnetic field. The molecular principal axes of $\hat{g}$ and $\hat{A}$ tensors are x, y, z. The laboratory frame is X, Y, Z (Z optical axis, see Figure 2). g and hyperfine components in the $\mathbb{B}$ direction are to be expressed in terms of the components in the x, y, z frame. For rapid molecular motions, the

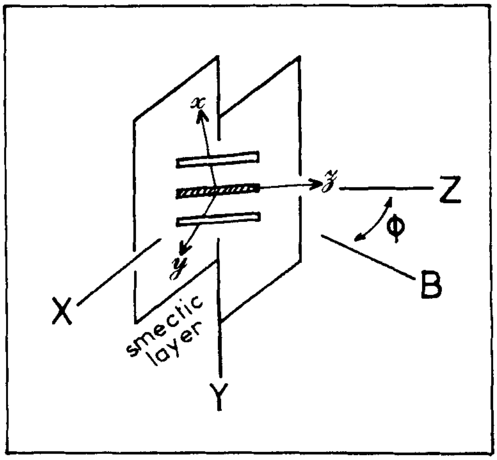


FIGURE 2 Probe molecular frame (x, y, z) and laboratory frame (X, Y, Z). In oriented samples, the smectic layers are vertical; the direction of the optical axis Z makes an angle ϕ relative to the horizontal magnetic field B.

Hamiltonian should be time averaged. Then, the observed g factor and hyperfine anisotropies, in the field direction, are:

$$\langle g \rangle - g = \tfrac{2}{3}[S_{xx}g_{xx} + S_{yy}g_{yy} + S_{zz}g_{zz}] \tag{2}$$

$$\langle a \rangle - a = \tfrac{2}{3}[S_{xx}A_{xx} + S_{yy}A_{yy} + S_{zz}A_{zz}] \tag{3}$$

Here, S_{ii} $(i = x, y, z)$ are the order parameters, that is the averages: $S_{ii} = \tfrac{1}{2}\overline{(3\cos^2\theta_i - 1)}$ (θ_i fluctuating angle between the ith axis and the field direction); g and a are isotropic values:

$$\tfrac{1}{3}(g_{xx} + g_{yy} + g_{zz}) \quad \text{and} \quad \tfrac{1}{3}(A_{xx} + A_{yy} + A_{zz}).$$

In nematics, because of the nitroxide $\hat{A}$ tensor axial symmetry ($A_{zz} = A_{\parallel}$, $A_{xx} = A_{yy} = A_{\perp}$) and of the S_{ii} zero sum property, it follows from Equations 2 and 3:

$$S_{zz} = \frac{3}{2}\frac{\langle a \rangle - a}{A_{\parallel} - A_{\perp}} = \frac{\langle a \rangle - a}{A_{\parallel} - a} \tag{4}$$

$$S_{xx} = \frac{3(\langle g \rangle - g) - 2S_{zz}(g_{zz} - g_{yy})}{2(g_{xx} - g_{yy})} \tag{5}$$

$$S_{yy} = -S_{xx} - S_{zz} \tag{6}$$

In oriented smectics, assuming cylindrical motion and taking the field either parallel to the axis of motional averaging ($\langle g \rangle = \overline{g}_{\parallel}$, $\langle a \rangle = \overline{A}_{\parallel}$), either perpendicular to it ($\langle g \rangle = \overline{g}_{\perp}$, $\langle a \rangle = \overline{A}_{\perp}$), the nine non zero values of the order matrix $S_{ii}^{\eta\eta}$ $(\eta = X, Y, Z)$ may be determined by analogous expressions.

The splitting and g factor angular dependences, when the magnetic field makes an angle ϕ with the axis of motional averaging, are:

$$\langle a \rangle(\phi) = \sqrt{\overline{A}_{\parallel}^{2}\cos^2\phi + \overline{A}_{\perp}^{2}\sin^2\phi} \tag{7}$$

$$\langle g \rangle(\phi) = \sqrt{\overline{g}_{\parallel}^{2}\cos^2\phi + \overline{g}_{\perp}^{2}\sin^2\phi} \tag{8}$$

It is worthwhile to recall that such an analysis of the spectra requires axially symmetric and fast motions. The first point will be discussed in the last section. The second requirement is not fulfilled in every case: for large probes I and II in low temperature smectic mesophases, the e.s.r. spectra are clearly typical of slow motion (cf. Figure 4a). Freed *et al.*[11] have developed a theory for detailed spectrum analysis in the slow tumbling region. Such an analysis is then necessary to get the correct magnitudes of the order parameters which cannot be simply deduced from the line positions as in the motional narrowing region; moreover, that last extrapolation should be handled with care when looking at the transition temperatures (the smectic

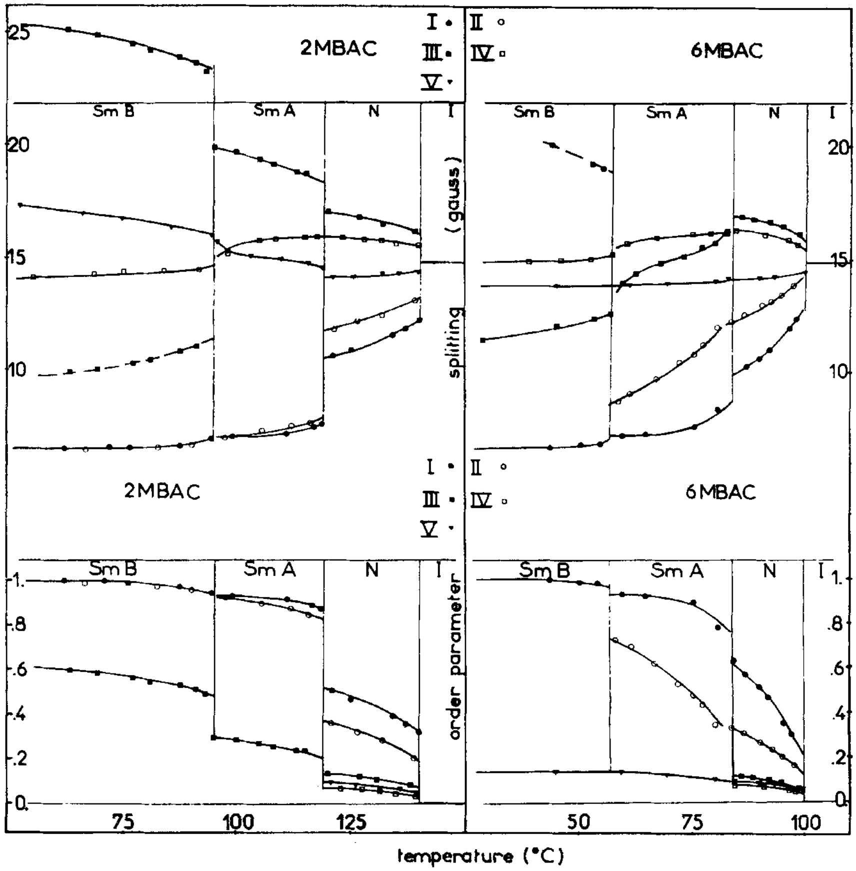


FIGURE 3 Temperature dependences of the splitting $\langle a \rangle$ and of the probe long axis order parameter S. For clarity, the isotropic splitting of probe I in 2MBAC, 14.9 Gauss, is taken as a reference and for each probe the quantity represented is $\langle a \rangle(14.9/a_{\mathrm{iso}})$ with a_{iso} the actual value of "a" measured in the isotropic phase of the given liquid crystal. In 2MBAC, $a_{\mathrm{iso(I)}} = 14.9$G; $a_{\mathrm{iso(II)}} = 14.75$G; $a_{\mathrm{iso(III)}} = 14.75$G; $a_{\mathrm{iso(IV)}} = 15.1$G; $a_{\mathrm{iso(V)}} = 15.75$G. In 6MBAC, $a_{\mathrm{iso(I)}} = 15.15$G; $a_{\mathrm{iso(II)}} = 14.9$G; $a_{\mathrm{iso(III)}} = 14.45$G; $a_{\mathrm{iso(IV)}} = 14.55$G; $a_{\mathrm{iso(V)}} = 15.6$G. Dashed lines correspond to "$\perp$" signal when two signals coexist. The order parameter S is represented only for the "$\parallel$" signal; cylindrical symmetry is assumed and no correction is made to take account of the angle between long axis and molecular axis for probes I, II, and V.

A ↔ smectic B temperature of 6MBAC deduced from probe II E.S.R. spectra examination in Reference 2 was erroneous). However, because we are only interested in comparison of the various probes behaviour, in every case we calculate the order parameters as described above for fast motions and use them as indicative parameters in a temperature diagram such as Figure 3. On the same grounds, no correction is included to take account of non coincidence between the motional axis and molecular axis.[5]

III RESULTS AND DISCUSSION

1 Nematic mesophases

For probes I, II and V, S_{zz} is negative with a minimum $= -0.5$ because the z axis is preferentially perpendicular to the optical axis; for probes III and IV, S_{zz} is positive with a maximum $= 1$ because the z axis is preferentially parallel to the optical axis. For comparison, we used for each probe the order parameter of the molecular axis aligned by the director $S \simeq S_{yy} = -2S_{zz}$ for I and II, $S = S_{zz}$ for III and IV, $S \simeq S_{xx} = -2S_{zz}$ for V.[5] The temperature dependences $\langle a \rangle(T)$ and $S(T)$ are shown in Figure 3. As qualitatively expected, the highest S (smallest amplitude of fluctuations) are obtained with rigid and long shaped probes I and II: $S_{\mathrm{I}} > S_{\mathrm{II}} > S_{\mathrm{III}} > S_{\mathrm{V}} > S_{\mathrm{IV}}$ in a given liquid crystal. For a given probe, all along the nematic range, the shorter the mesomorphic compound chain length, the higher the order parameter S.

2 Smectic mesophases

Typical spectra in oriented smectic A and B are shown in Figure 4. These spectra display three types of signals classified as follows:

a) The signal referred as "‖" corresponds to a mean orientation of the probe long axis parallel to the optical axis. The degree of order S is positive as in the nematic.

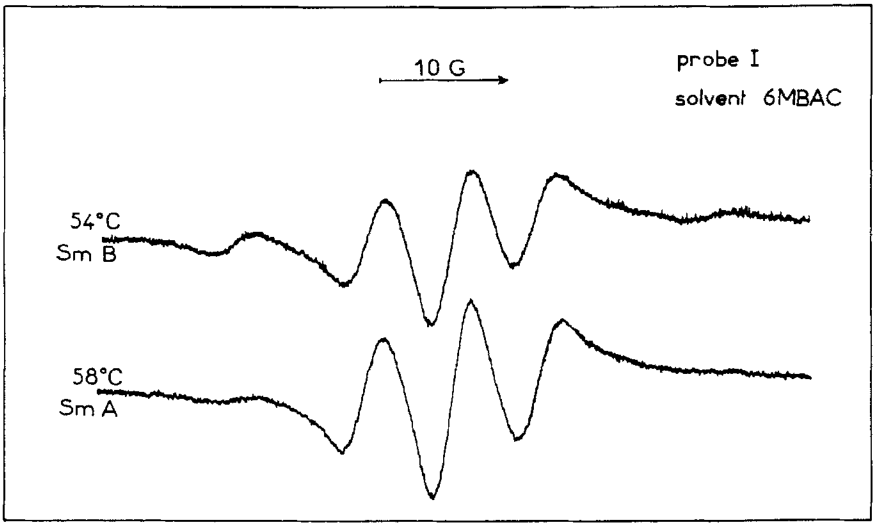


FIGURE 4a "‖" E.S.R. signal for cholestane dissolved in 6MBAC smectic A mesophase; coexistence of "‖" and "⊥" signals in smectic B. Partial aggregation of the probe gives a broad one line spectrum which contributes to the overall spectrum.

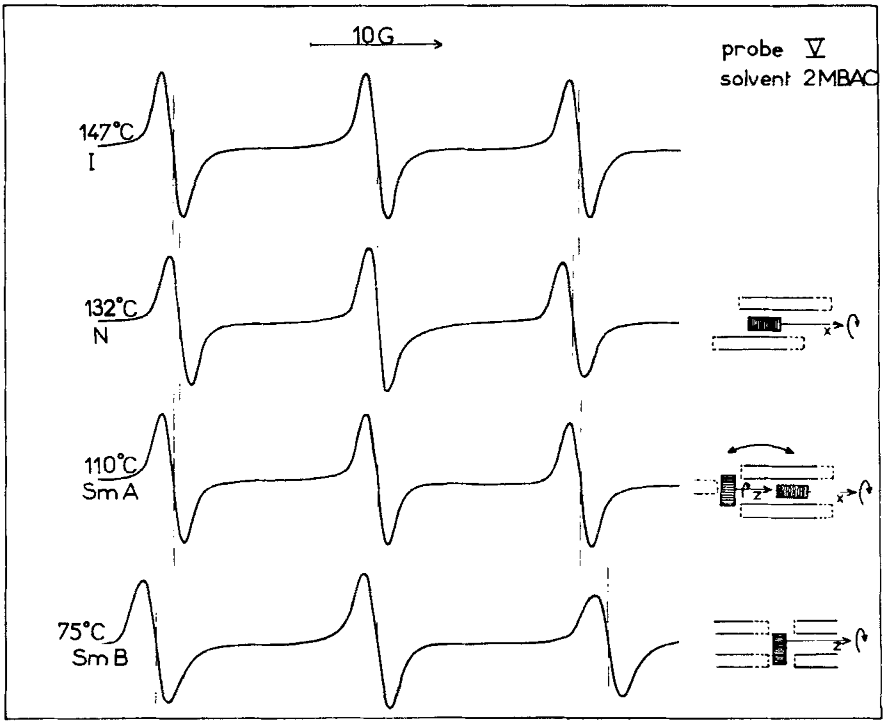


FIGURE 4b E.S.R. spectra of probe V dissolved in various phases of 2MBAC. "Intermediate" signal takes place in smectic A mesophase and "⊥" signal in smectic B. For clarity, the central line is fixed; in fact, it moves towards high fields when the temperature is lowered ($\langle g \rangle$ decreases). On the right, schematic representation of the probe (▥) location and motion; the mesomorphic molecule is made of a rigid part (continuous line) and a flexible part (broken line).

b) The signal referred as "⊥" corresponds to a mean orientation perpendicular to the optical axis. S is negative.

c) The signal referred as "intermediate," with three hyperfine lines in any direction, is characterized by an unusual temperature dependence of S: the order decreases with temperature.

The "⊥" signal appears in smectic phases, mainly B phases; it is never observed in nematics.[6] An optical examination under microscope demonstrates that it does not arise from macroscopic heterogeneities inside the sample: for probe I in 6MBAC the "⊥" signal becomes significant only in smectic B, but the overall texture is identical in both mesophases. Furthermore, the ratio "⊥" spins over "∥" spins, when both signals coexist, is independent of the sample preparation. A special probe conformation could not explain any more the "⊥" signal existence, since probes as rigid as probes I and II exhibit this orientation. Thus, we must assume the existence, in smectic phases, of a second site able to accommodate the probe under conditions depending on solute and solvent molecules. Due to the structure of the smectic, we are led to consider the "$\|$" signal as a result of alignment by the rigid aromatic core ("$\|$" site) and the "$\perp$" signal as a result of probe intercalation between the smectic layers in the region of the flexible alkyl chains ("$\perp$" site). Then, the "intermediate" signal corresponds to an equilibrum between two states or alternatively to an intermediate site. The role played by the flexible chain in the perpendicular orientation of the probe is confirmed by the observation previously mentioned[2]: for probe II in smectic B phases of the *n*-MBAC series where both "$\|$" and "$\perp$" signals coexist, the ratio "$\perp$" over "$\|$" spin populations increases from 0 to 50% when the number *n* of carbon atoms of the chain increases from 2 to 6.

In smectics, on the basis of the two sites hypothesis, behaviour of the probe arises from its location in aromatic nuclei site or in alkyl chains site. All the observations are summarized in Table I.

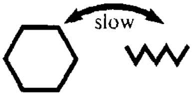
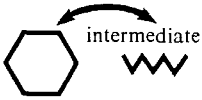
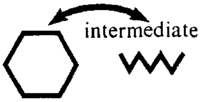
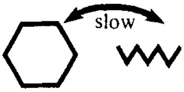
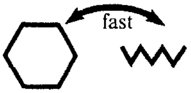
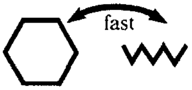
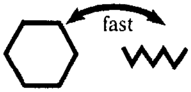
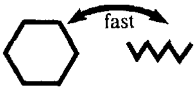
a) The probe molecule is long and rigid (probes I and II). Its long axis orientation is mainly parallel to the optical axis (probes I and II in 2MBAC smectic A and B, probe I in 6MBAC smectic A). However, when the alkyl chain of the host molecule is long enough (6MBAC), the chain site is also available. Two classes of spectra are obtained depending on the value of the exchange frequency ν_e between both sites. When ν_e is slow in comparison of the two signals separation ($\nu_e \ll 10^7$ Hz), "$\|$" and "$\perp$" signals coexist (probe I in 6MBAC smectic B); when ν_e is of the order of 10^7 Hz, a broad spectrum is observed (probe II in 6MBAC smectic A and B).

b) The probe molecule (V) is short and rigid. In the short chain compound 2MBAC, the probe is entirely (smectic B) or partially (smectic A) excluded from the aromatic rings site, probably because of strong lateral interactions between adjacent mesomorphic molecules. In the last case, rapid exchange frequency between both sites yields averaged spectra showing an unusual temperature dependence since the observed splitting is then a weighted average between a "$\|$" and a "$\perp$" splittings. In 6MBAC, the probe, probably because of weaker lateral interactions and of its disc shape, is accommodated by the "$\|$" site in both mesophases and the degree of order is very low.

c) The probe molecule is flexible (probes III and IV). The short probe IV is entirely accommodated in the chain site of the both compounds smectic B and partially with a short time of residence in smectic A: lateral interactions exclude the probe at low temperatures. The long probe III finds total accommodation in the chain site of 6MBAC smectic B but only partial accommodation in other cases. This behaviour could be explained by interlayer correlations[7] which decrease with increasing chain length, making easier the probe intercalation.

TABLE I

Probe localization in smectic A and B mesophases.

	solvent			
	2MBAC		6MBAC	
probe	Sm A	Sm B	Sm A	Sm B
I	 "∥" signal	 "∥" signal	 "∥" signal (weak "⊥" signal)	 "∥" + "⊥" signals (~80%) (~20%) $\nu^{e} \ll 10^7$ Hz
II	 "∥" signal	 "∥" signal	 broad signal $\nu_e \sim 10^7$ Hz ν_e decreases with T; two signals—one "∥", one isotropic—overlap	 broad signal quasi isotropic splitting.
III	 "intermediate" signal broad high field line $\nu_e \gtrsim 10^7$ Hz	 "∥" + "⊥" signals (50%) (50%) important partial aggregation $\nu_e \ll 10^7$ Hz	 "intermediate" signal $\nu_e \gg 10^7$ Hz	 "⊥" signal
IV	 "intermediate" signal $\nu_e \gg 10^7$ Hz	 "⊥" signal	 "intermediate" signal little temperature dependence of $\langle a \rangle$ $\nu_e \gg 10^7$ Hz	 "⊥" signal quasi isotropic splitting.
V	 "intermediate" signal $\nu_e \gg 10^7$ Hz	 "⊥" signal	 "∥" signal very low splitting anisotropy.	 "∥" signal very low splitting anisotropy.

Sites: ⬡ rigid central cores; 〰 flexible and chains.

3 Transitions

The description of both sites allows the following interpretation: in the "$\parallel$" site, the hyperfine splitting reflects the orientational order of the mesomorphic molecules long axes and in the "$\perp$" site it is related to the chain fluidity. Examination of the splitting discontinuities at the transitions then gives both kinds of information when suitable probes are used (I or II for aromatic cores, III or IV for end chains).

No information on the solid phase is available because of probe exclusion from crystalline lattice and aggregation. However, the high values of the order for probe I and II in the "$\parallel$" site of both smectic phases suggest there is no important orientational order change at the solid $\rightleftarrows$ smectic and smectic A $\leftrightarrow$ smectic B transitions. On the other hand, at this last transition, relatively large discontinuities are exhibited by flexible probes in the "$\perp$" site. That would mean the chains are not completely melted[8] in the smectic B phase, and smectic B $\rightarrow$ smectic A transition is accompanied by further release of the chain motions. In contrast, at the smectic A $\rightarrow$ N transition loss of translational order influences much more the orientational order of the rigid part of the molecule than the fluidity of the chains.

IV PROBE MOTIONAL AXIS IN THE "$\perp$" SITE

The "$\parallel$" E.S.R. signal shows the usual angular dependence when rotating the sample in the magnetic field (see Equations 7 and 8). The observed hyperfine splitting and g factor in two perpendicular directions at a given temperature give the extreme values $\bar{A}_{\parallel}$, $\bar{A}_{\perp}$, $\bar{g}_{\parallel}$, $\bar{g}_{\perp}$.

The "$\perp$" signal shows a similar angular dependence. However the extreme values of the splitting and of the g factor are not those of the "$\parallel$" signal when both signals coexist at a given temperature. This is illustrated on Figure 5 for probe III in 2MBAC at 85°C (smectic B) $\bar{A}_{\parallel} = \bar{A}_{\max} = 23.8\text{G}$, $\bar{A}_{\perp} = \bar{A}_{\min} = 10.3\text{G}$ for the "$\parallel$" signal, whereas $\bar{A}_{\max} = 17\text{G} = \langle a \rangle(90°)$, $\bar{A}_{\min} = 10.2\text{G} = \langle a \rangle(0°)$ for the "$\perp$" signal. This trend is observed for each probe in any compound of the studied series wherever both signals coexist. This could be due to a probe inclination on the XZ plane (see Figure 2), in the "$\perp$" orientation. To elucidate this point, powder spectra are needed. We used probe V in 2MBAC because it is rigid, the "$\perp$" signal is alone in smectic B mesophase and the order is large enough. The spectra show a not quite isotropic distribution. However two stationary values of the splitting can be measured (Figure 6); they well fit the extreme values $\langle a \rangle(0°)$ and $\langle a \rangle(90°)$ measured in oriented samples along Z and X axes respectively (Table II). Then, we conclude that these axes are stationary directions. In order to

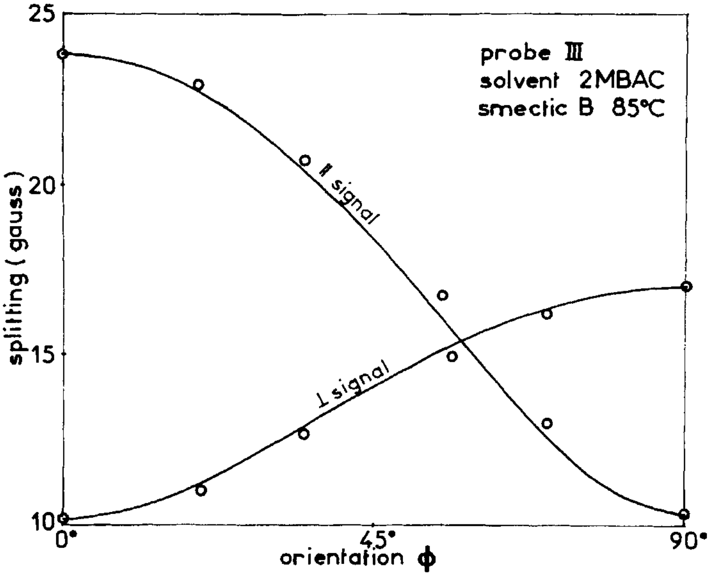


FIGURE 5 Splitting angular dependence. The experimental values are very inaccurate in the area of $\phi = 60^\circ$ because of the two signals overlapping. Simultaneously, the observed g factor varies from $\bar{g}_\parallel = 2.00449$ to $\bar{g}_\perp = 2.00684$ for the "∥" signal, and from 2.00698 to 2.00542 for the "⊥" signal, when ϕ increases from 0° to 90°.

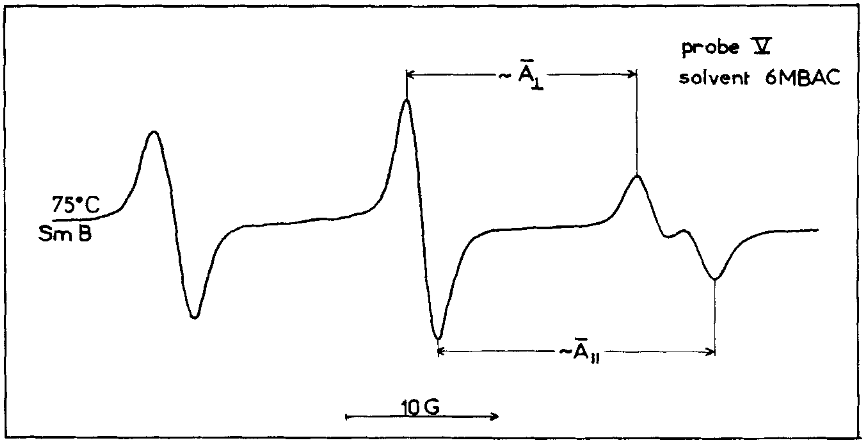


FIGURE 6 Powder spectrum for the "⊥" signal.

TABLE II

Probe V in 2MBAC smectic B

	splitting (Gauss)				
	oriented samples		powder sample		
T(°C)	$\langle a\rangle(0°)$ $B\parallel Z$	$\langle a\rangle(90°)$ $B\parallel X$	$\bar{A}_{max}$	$\bar{A}_{min}$	$3a^{a} - \bar{A}_{max} - \bar{A}_{min}$
93°	17	15.4	17	15.25	15
84°	17.55	15.05	17.55	15	14.7
75°	17.75	14.95	17.85	14.8	14.6
68°	17.95	14.8	18.05	14.75	14.45
55°	18.3	14.65	18.5	14.5	14.25

[a] a is the experimental value measured in the isotropic phase; local environment acts on this value. However, the difference between the values in a chain environment and in the isotropic liquid is less than 0.5G.[9]

determine the third principal value of the motionaly averaged hyperfine tensor, let us look at the quantity $3a - \bar{A}_{max} - \bar{A}_{min}$: its value is close to $\bar{A}_{min}$. On this basis, we consider the motion in the "⊥" site as "quasi cylindrical" around a probe axis, z, parallel to the optical axis Z, with $\bar{A}_{max} = \bar{A}_{\parallel}$ and $\bar{A}_{min} = \bar{A}_{\perp}$. However, a complete analysis, with calculation of a new order parameter proportional to the difference $(S_{xx} - S_{yy})$, is needed to conclude about cylindrical symmetry. Figure 4 illustrates probe orientation and motion in both sites. The same analysis for the flexible probe III in 2MBAC smectic B shows that in the "⊥" site, the probe long axis is perpendicular to the director and motion takes place around a short axis aligned parallel to the director of the mesophase, and similarly for any probe in the "⊥" site (see Table III).

TABLE III

"⊥" signal in oriented smectic B mesophase. Evidence for rotation around a short probe molecular axis preferentially parallel to the optical axis. The splitting values are in Gauss.

	solvent									
	2MBAC (85°C)					6MBAC (53°C)				
probe	S^{ZZ}_{zz}	$\langle a\rangle(0°)$	$\langle a\rangle(90°)$	$a_{cal}{}^{a}$	a^{b}	S^{ZZ}_{zz}	$\langle a\rangle(0°)$	$\langle a\rangle(90°)$	$a_{cal}{}^{a}$	a^{b}
I						+0.25	19.2	12.9	15.0	15.15
II						0	15.0	15.0	15.0	14.9
III	−0.26	10.2	17	14.7	14.75	−0.14	12.05	15.75	14.5	14.45
IV	−0.03	14.6	14.9	14.8	15.1	+0.01	14.7	14.6	14.6	14.55
V	+0.11	17.4	15.35	16.0	15.75					

[a] $a_{cal} = \frac{1}{3}[\langle a\rangle(0°) + 2\langle a\rangle(90°)]$ assuming cylindrical motion.

[b] a: experimental value measured in the isotropic liquid.

Therefore, in contrast to the " ∥ " signal, the " ⊥ " signal does not correspond to a specific orientation of the probe long axis, but rather results from a motion average. That will be better seen when looking at the order parameters.

V ORDER PARAMETERS IN NEMATIC AND SMECTIC MESOPHASES

In order to determine the order parameters $S_{ii}^{\eta\eta}$ (see Equations 4, 5 and 6), g factor and hyperfine anisotropies were measured on e.s.r. spectra of two probes dissolved in the same mesomorphic compound 2MBAC: a rigid one probe II and a flexible one probe III.

The first probe gives good information on the "∥" site but g factor anisotropy is low because motion takes place around y axis ($\bar{g}_{yy} \simeq g_0$). The second one may be accommodated in both sites; the g anisotropy is large for this probe but two difficulties arise: in smectic A the exchange frequency between both sites is of the order of 10^7 Hz, no information can be obtained in this mesophase on the "⊥" site; in smectic B the exchange frequency is slow but partial aggregation of the probe molecules gives a broad line superimposed on the five lines spectrum of the dilute molecules hindering precise measurements of g factors. Because of these imprecisions, order parameters cannot be confided to more than 6.10^{-2} for probe II and 3.10^{-2} for probe III. Table IV lists the values in the three mesophases. Let us look first at androstane. The probe long axis is close to y axis. S_{yy}^{ZZ} is positive. The motion is cylindrical in the three mesophases or at least the anisotropy

TABLE IV

Order parameters for probes II and III dissolved in 2MBAC. The values in parentheses are those relative to the "⊥" site.

		mesophase						
		N (138°C)	Sm A (112°C)			Sm B (85°C)		
probe		$\eta = Z$	$\eta = X$	$\eta = Y$	$\eta = Z$	$\eta = X$	$\eta = Y$	$\eta = Z$
II	$S_{xx}^{\eta\eta}$	−0.11	+0.28	+0.13	−0.41	+0.24	+0.19	−0.43
	$S_{yy}^{\eta\eta}$	+0.22	−0.49	−0.36	+0.85	−0.50	−0.41	+0.91
	$S_{zz}^{\eta\eta}$	−0.11	+0.21	+0.23	−0.44	+0.26	+0.22	−0.48
III	$S_{xx}^{\eta\eta}$	−0.05			−0.13	+0.19	−0.07	−0.12
						(−*0.10*)	(−*0.16*)	(+*0.26*)
	$S_{yy}^{\eta\eta}$	−0.04			−0.08	+0.04	+0.38	−0.42
						(−*0.05*)	(+*0.06*)	(−*0.01*)
	$S_{zz}^{\eta\eta}$	+0.09			+0.21	−0.23	−0.31	+0.54
						(+*0.15*)	(+*0.10*)	(−*0.25*)

$|S_{xx}^{ZZ} - S_{zz}^{ZZ}|$ is not significant in account of imprecision. In smectic B mesophase, at 85°C, S_{yy}^{ZZ} is close to maximum value 1, S_{xx}^{ZZ} and S_{zz}^{ZZ} are close to -0.5, thus x and z molecular axes lie preferentially in a plane perpendicular to Z (parallel to the smectic layer). When the magnetic field is along X, S_{yy}^{XX} is close to -0.5 and S_{xx}^{XX}, S_{zz}^{XX} close to $+0.25$ because for isotropic motion in a plane $\overline{\cos^2 \theta} = -0.5$. As a consequence, the probe motion is cylindrical around its long axis in the aromatic core site of smectic B. That could mean two things: lateral order does not induce motion anisotropy or such an anisotropy exists but cannot be detected because of dynamical rearrangements of polydomains in the smectic plane due to the absence of privilegiate axis in this plane for an uniaxial smectic B.

For the flexible probe III in the "$\|$" site, S_{zz}^{ZZ} is positive, motion taking place around z axis, and it increases with decreasing temperature. Anisotropy $S_{yy}^{ZZ} - S_{xx}^{ZZ}$ is very low in nematic, increases in smectic A and becomes large in smectic B ($S_{yy}^{ZZ} - S_{xx}^{ZZ} \simeq 0.55\, S_{zz}^{ZZ}$). However, the results for androstane show that this anisotropy is not due to an intrinsic property of the smectic B mesophase but rather to the probe flexibility which leads to a conical motion[10] of the nitroxide group, z axis remaining preferentially aligned parallel to the optical axis and y axis preferentially in the YZ plane parallel to Y axis ($S_{yy}^{YY} > 0.25$). The lower the temperature, the larger the motion anisotropy.

In the "$\perp$" site, x axis is preferentially parallel to the optical axis Z with a low order parameter. When looking along X axis, z seems preferentially parallel to it but with an order parameter $S_{zz}^{XX} < 0.25$; moreover S_{zz}^{YY} is also positive. That confirms motion around the short axis x, the probe long axis z remaining close to the smectic layers with no preferred direction.

VI CONCLUSION

This work contributes to extend the field of spin probes used in structural studies of thermotropic liquid crystals. Following points are to be noted:

1) The spin probes have not a unique orientation in smectic mesophases. This is attributed to the existence of at least two sites. One site constituted by interacting aromatic nuclei allows probe insertion parallel to the mesomorphic molecules; the other site constituted by the fluid alkyl chains allows probe intercalation between the smectic layers.

2) The rules of probe insertion in these sites are deduced from the study. The best way to explore the aromatic core site is to choose a probe molecule rigid, of length close to the length of the rigid part of the mesomorphic molecule. Total insertion in this site requires two fulfilments: relatively weak

lateral interactions (high temperature smectic) or strong longitudinal correlations between smectic layers (short chain mesomorphic compound). Between total insertion and total exclusion from the rigid core site, intermediate situations occur where both sites are able to accommodate the probe; the time of residence in a site is shorter for smaller probes at higher temperatures.

3) For the compounds of the studied series with monotropic smectic B mesophases, the chains are not perfectly melted in the smectic B: the order of a probe intercalated between the smectic layers decreases with increasing temperature. A modification of the chains fluidity occurs at the smectic B ↔ smectic A transition.

4) In smectic B with intraplanar translational order, no rotational anisotropy of the rigid probes motion is detected.

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