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SMECTIC *E*, *C* AND *A* FREE RADICALS

M. DVOLAITZKY,* J. BILLARD* and F. POLDY†
Laboratoires de Chimie Organique des Hormones‡ et de Physique de la Matière Condensée,§ Collège de France,
75231 Paris Cedex 05, France et Laboratoire de Dynamique des Cristaux Moléculaires,§ 59650 Villeneuve d'Ascq,
France

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Abstract—Some new paramagnetic liquid crystals are described. Their mesophases have been identified, by isomorphism with known phases, as smectic mesophases of types S_E, S_C and S_A.

A convenient method for the study of the static and dynamic structure of a liquid crystal by ESR involves the use of spin labelled molecules present at low concentration in an unlabelled liquid crystalline matrix. We have studied a number of features of the smectic polymorphism of 4,4'-octadecyloxyazoxybenzene by means of a series of spin labels very closely related to the host molecule.[1]

It is frequently pointed out that the precise physical interpretation of measurements on spin-labelled molecules is impaired by the fact that the label is slightly different from the host molecule. If the spin labels themselves were mesomorphic substances, the ESR technique would give "true" information about the mesophases. This was our purpose when we prepared for the first time free-radical liquid crystals which possess the smectic-*C* type mesophase.[2] In order to obtain free-radical materials presenting smectic-*A* (S_A) phases, a paramagnetic oxazolidinyl-2-N-oxy group was substituted on the alkoxy chains of substances belonging to series known to form S_A phases.

2-*Acyl-7-alkoxy fluorenes*

2-Acyl-7-alkoxy fluorenes are known to present S_A phases.[3] In order to check the effect of a long alkoxy chain, 2-heptanoyl-7-hexadecyloxy fluorene was prepared. It possesses a stable S_A phase between 105–106° and 130–131°C. The substitution, at C-8 of the alkoxy chain of the paramagnetic oxazolidinyl-2-N-oxy group gives a racemic mixture which melts at 76–83°C and possesses only a metastable S_A phase below 68–69°C. The substitution thus considerably reduces the stability domain of the mesophase. In order, therefore, to obtain free-radical substances with stable mesophases it seems preferable to start with materials possessing mesophases over as large as possible a temperature interval.

2-(4-*Alkoxy biphenyl*)-*quinoxalines*

The 2-(4-alkyl and alkoxy-biphenyl)-quinoxalines present S_A phases over a large temperature range.[4] The member of this series with the longest known chain (p-decyloxy) possesses S_E and S_A phases.[5] In order to check that increasing chain length does not suppress this mesomorphic character, 2-(4-hexadecyloxy biphenyl)-quinoxaline **6** was prepared. It presents a S_A phase from 109 to 182.5°C and a metastable S_E phase below 106°C. The compound **6** and the corresponding free radicals **8**, **9** and **10** (Table 1) were all prepared from the 2-(4-hydroxybiphenyl)-quinoxaline **5** by condensation with hexadecylbromide or appropriate "spin-labelled" tosylates **7**.[2]

The compound **5** was obtained from 4-hydroxybiphenyl **1** through 4-acetoxy-4'-acetyl-biphenyl **2** (prepared by the Friedel–Crafts reaction) which was oxidized by selenium dioxide to the glyoxal derivative **3** and then transformed to quinoxaline **4**.

The identification of the mesophases is described later in this paper. The transition $S_C \longleftrightarrow S_A$ of **10** was not detected in the calorimetric analysis with a Perkin Elmer DSC-2, but was detected by electron spin resonance (ESR) spectroscopy.

Identification of the mesophases

The phases were identified by establishing their isomorphy with known phases in other substances.[6] The form of the isobaric phase diagrams of the mixtures of the known and unknown materials were determined by the contact method.[7]

The phase diagram **a** (Fig. 1) of mixtures of **6** with ethyl p-terphenyl 4,4'-dicarboxylate **11** (which forms S_E and S_A mesophases[8] shows that **6** has S_A and (S_E) mesophases.

Diagram **b** (Fig. 1) of mixtures of **10** with n-butyl-4-n-heptyloxy-4'-benzylidene)-aniline **12** (which presents S_E, S_C, S_A and nematic mesophases[9] shows that **10** possesses S_A and S_C mesophases. The $S_A \longleftrightarrow S_C$ transition in this phase diagram could not be detected with certainty for all mixture ratios under the polarising microscope as it was marked only by the appearance of faint transition bars on the focal conic texture. The transition spindle was therefore confirmed by means of the ESR spectra (see below) which establish the points marked on the diagram.

The diagram **c** (Fig. 1) of mixtures of **10** and **6** confirms the identification of the S_A phase in **10** and shows that it also possesses a S_E phase. The mesophases thus identified in **10** were then used for the identification of those of the other two substances in Table 1. The diagram **d** (Fig. 1) of mixtures of **10** and **9** shows that **9** presents metastable (S_A) and (S_C) phases. The diagram **e** (Fig. 1) of mixtures of **10** and **8** shows that the latter forms stable S_A and S_E phases.

Phase diagram determination by ESR

The fact that **10** is a stable free radical enables it to be studied by means of ESR. The high concentration of unpaired electron spins (one per molecule in pure **10**) gives rise to ESR spectra dominated by exchange

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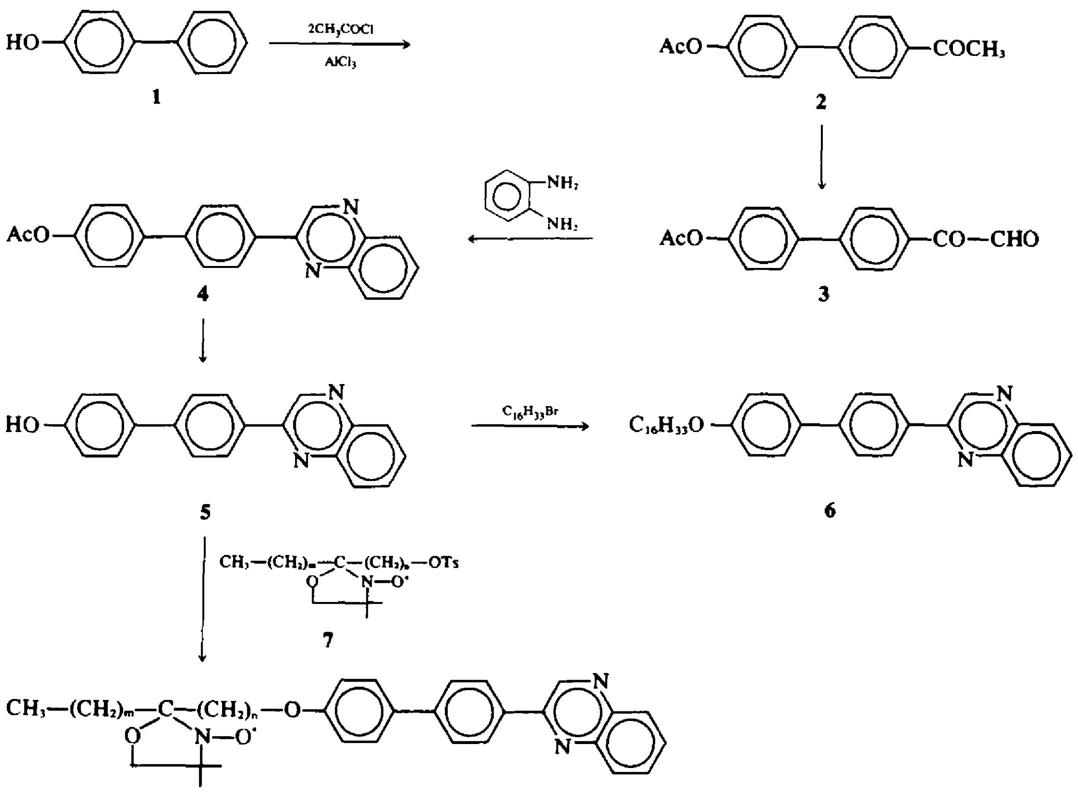
†Present address: Research School of Chemistry, Australian National University, Canberra, Australia.

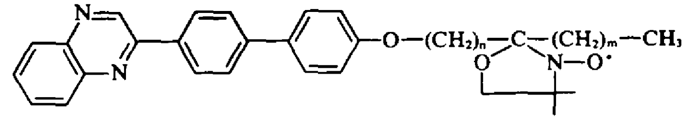
‡Groupe de recherches du C.N.R.S.

§Equipes associées au C.N.R.S.



8: n = 8, m = 0
9: n = m = 4
10: n = m = 7

Table 1. Liquid crystalline p-biphenyl-p′-quinoxalines free radicals



No.	n	m	k ⟶ S_E	S_E ⟶ S_C	S_C ⟶ S_A	S_A ⟶ L
8	8	0	97–113		118–123	155–158.5
9	4	4				116–118
					(100–101)	(104–108)
10	7	7	66–79	92–99	117–119	130–134

The temperatures are indicated in °C. The values in brackets refer to monotropic transitions.

interaction and consisting of a single broad line. In oriented samples (homeotropic in S_A—smectic planes parallel) the peak-peak derivative linewidth is highly anisotropic being given approximately by the relation $\alpha + \beta(3\cos^2\theta - 1)^2$ where θ is the angle between the applied magnetic field and the normal to the smectic layers. In the temperature range of the smectic phases α is weakly and β strongly temperature-dependent. The line shape is also anisotropic being Lorentzian at the "magic angle" ($3\cos^2\theta - 1 = 0$) and considerably non-Lorentzian at other angles. This behaviour is characteristic of ESR spectra dominated by the exchange interaction acting in two dimensions.[10] A more detailed account will be given in a future article. In this work we have simply used the temperature dependence of the ESR line width at $\theta = 0$ of mixtures of **10** with **12** as a means of detecting the phase transition and establishing the phase diagram.

Three samples of different molar composition were prepared by weighing the appropriate small (~0.1–0.4 mg) quantities of **10** and **12** on a microbalance accurate to ~5 μg. These were dissolved in a few drops of chloroform at the bottom of a small glass tube and the solution allowed to evaporate. The deposit was sheared between glass slides a few degrees below the clearing point in the S_A phase to produce a uniformly homeotropic sample whose ESR spectra were recorded as functions of temperature with the magnetic field perpendicular to the glass slides.

On plots of the linewidth versus temperature, the phase transitions show up as discontinuities in the value or slope. The corresponding transition temperatures and molar ratios are plotted in Fig. 1b.

Although the substitution of the paramagnetic oxazolidinyl-2-N-oxy group considerably reduces the

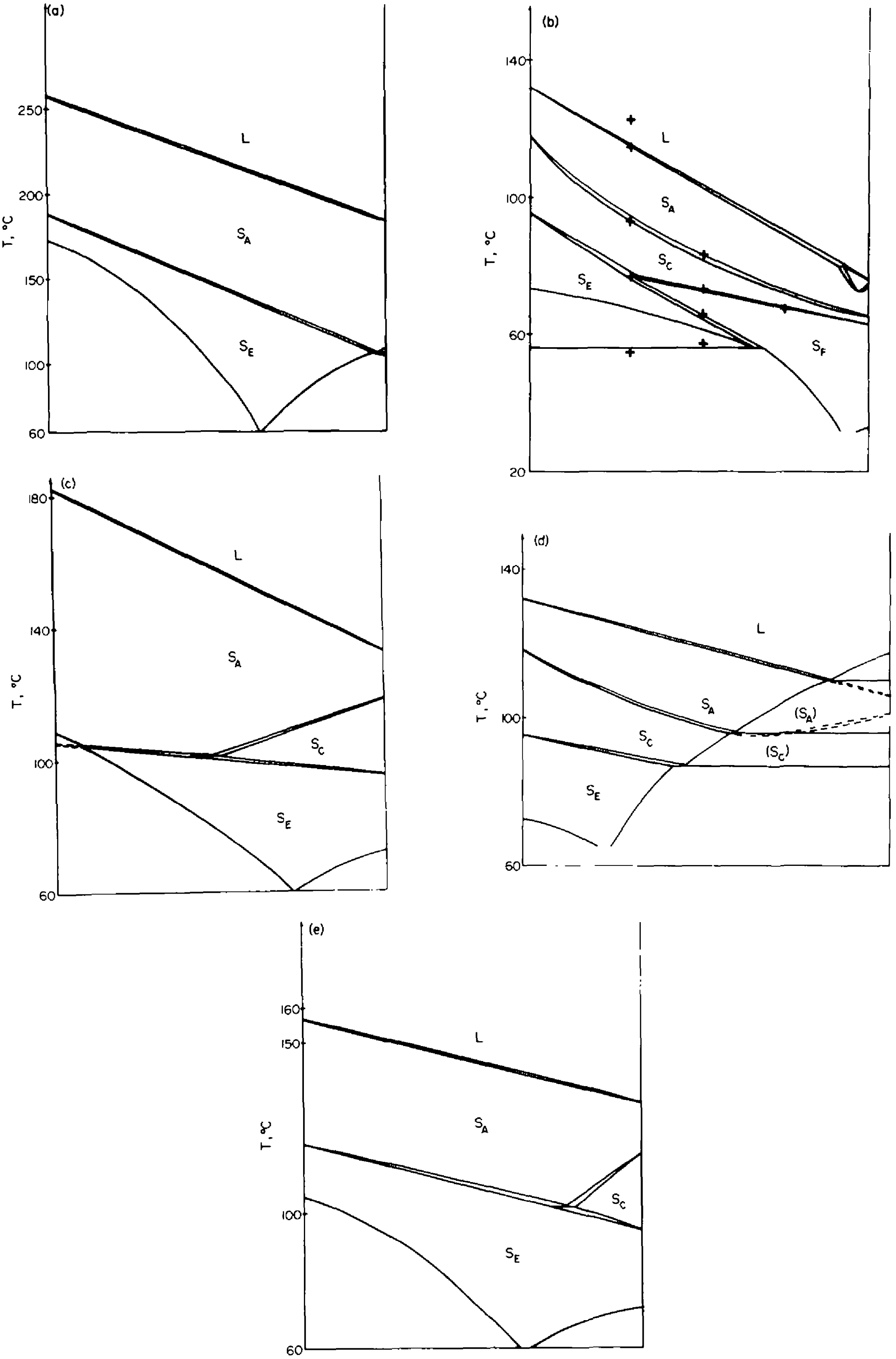


Fig. 1. Schematic isobaric phase diagrams for mixtures of compounds. (a) **11** (left) and **6** (right); (b) **10** (left) and **12** (rigt). The experimental points near the mixtures ratios 30 : 70, 50 : 50, and 75 : 25 are the transitions detected in the ESR spectra; (c) **6** (left) and **10** (right); (d) **10** (left) and **9** (right); (e) **8** (left) and **10** (right). The compound numbers are those of text and Table 1.

domain of existence of the mesophases it is possible by this method to obtain free radicals with S_F, S_C and S_A mesophases which are thermodynamically stable at atmospheric pressure. These mesophases can thus be studied *directly* by ESR. One of the materials described **10** is the first example of a S_F phase directly followed by S_C and of the coexistence of S_E and S_C stable phases in a pure compound.

EXPERIMENTAL

Preparation of materials

4-*Acetoxy*-4′-*acetylbiphenyl* **2**. A mixture of 4-hydroxybiphenyl **1**, (17 g; 0.1 mole) and aluminium chloride (2.67 g; 0.2 mole) in 20 ml of carbon disulfide was refluxed while stirring. Then 14.2 ml of acetyl chloride (0.2 mole) was added dropwise. After the mixture, initially clear, had been stirred and refluxed for 45 min, a brown resin formed. The liquid phase was separated and the solid residue hydrolysed by ice-hydrochloric acid; the resulting solid was collected and washed with water and ether to afford 20.27 g of **2** which was recrystallised in 200 ml of methanol to give plates, 9.54 g, m.p. 125–128°.

4-*Acetoxy*-*biphenyl*-4′-*glyoxal* **3**

To a stirred solution of selenium dioxide (1.475 g; 0.013 mole) in 20 ml of dioxane and 0.35 ml of water, was added 3.35 g of ketone **2** (0.013 mole). The reflux was continued for 4 h. After cooling, the solution was filtered, and evaporated in vacuo to afford 2.31 g of **3** after recrystallisation from a mixture of 75 ml of acetone and 125 ml of water.

2-(4-*Acetoxybiphenyl*)-*quinoxaline* **4**

To a suspension of **3** (600 mg) in ethanol was added an alcoholic solution of o-phenylenediamine. The mixture was warmed until dissolution occurred and needles of **4** formed, 0.660 g, m.p. 197–199°.

2-(4-*Hydroxybiphenyl*)-*quinoxaline* **5**

The saponification of **4** by refluxing for 30 min in methoxyethanol with conc NaOH, affords after addition of conc HCl until the red colour was transformed to orange and dilution with water, 0.317 g of **5**, fine needles, m.p. 237–239°. The recrystallisation from a mixture of ethanol, 5 ml and methoxyethanol, 5 ml give 0.227 g of **5**, m.p. 238–239°. Calc. for $C_{20}H_{14}N_2O$: C, 80.51; H, 4.73; N, 9.39. Found: C, 80.40; H, 4.71; N, 9.56%.

2-[4-(8-*Oxazolidinyl*-*N*-*oxy*)*hexadecyloxybiphenyl*]-*quinoxaline* **10**

To a suspension of **5** (68 mg; 0.23 mmole) in 4 ml of absolute ethanol, was added 0.25 ml of a mmolar alcoholic solution of sodium ethoxide; the alcohol was then removed *in vacuo* and replaced by a solution of the tosylate **7** (n = m = 7; 124 mg) in 4 ml of dry dimethylformamide. The mixture was warmed until the red colour changed to yellow (about 30 min). The solution was diluted with water and methanol and the solid collected was purified by TLC on silica gel with a mixture of ethylacetate–hexane (3:7). After three developments of the plate a yellow resin was eluted which was crystallised in methoxyethanol. One more crystallisation in isopropylalcohol afford **10** collected by centrifigation. (Calc. for $C_{40}H_{52}N_2O_3$: C, 77.13; H, 8.415; N, 6.75. Found: C, 77.23; H, 8.46; N, 6.90%).

2-[4-*Hexadecycloxybiphenyl*]-*quinoxaline* **6**

Prepared as for **10**. Recrystallised from methoxyethanol.

Textures

The substances were examined between glass slide and cover slip under a polarizing microscope with heating stage. Because of the high viscosities of the S_E and S_C phases their textures could only be observed on cooling. The textures of the S_A phases are of the focal conic type; those of **6**, **8** and **9** having a strong tendancy to homeotropy. In the smectic *C* phase those areas previously occupied by the homeotropic S_A, are birefringent (schlieren texture) while those arising from the S_A focal conics present modified focal conics with superimposed "paving". In the S_E phase those regions arising from the previously homeotropic S_A are birefringent with a schlieren or a mosaic texture, while the regions originating from the S_A focal conics present focal conics with transverse stripes or concentric arcs. The crystals obtained by cooling 2-heptanoyl-7-hexadecyloxy-fluorene and the compound **6** exhibit a pseudomorphosis of the focal conics.

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