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X-ray diffraction studies of binary mixtures of rod-like and biforked mesogenic molecules

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Two binary mixtures of a liquid-crystalline biforked molecule with derivatives of the *p*-terephtaldehyde-bis-alkyl-anilines have been studied. The phase diagrams as determined by differential thermal analysis and optical observations show a continuous miscibility in the nematic and smectic C phases. Information on the molecular conformation of the biforked molecules is derived from X-ray diffraction studies of the binary mixtures.

1. Introduction

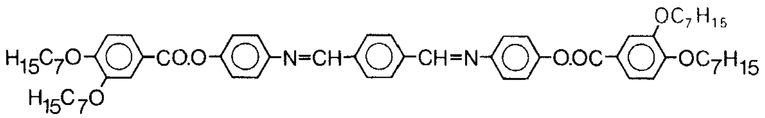
Studies of binary mixtures of mesogenic molecules offer a wide field of investigation since nematogenic or smectogenic pairs of compounds are, in general, totally miscible in the liquid-crystalline phases. This property was first used for the purpose of phase identification [1]. Moreover, the existence of a large domain of miscibility in the liquid-crystalline state gives us an opportunity to check the validity of additivity laws for many physical properties. In smectics, the fundamental feature is the occurrence of a one dimensional modulation of the density. The period is generally equal to the molecular length for pure compounds in a smectic A (S_A) state and varies linearly with the molar composition of the binary mixture. This Vegard law can be applied to a pair of molecules with a large difference in length (up to 30 per cent) [2] which confirms three important properties of the molecules in a smectic mesophase:

(i) The cross-section of the molecules in the layer plane is the same for all of the rod-like molecules and for the two constitutive parts of these molecules (i.e. the aromatic and aliphatic moieties).
(ii) The specific volume of a methylene group in a smectic phase is nearly constant [3].
(iii) the linear dependence of the lattice spacing over a large range of concentration is a consequence of the segregation between the aromatic and paraffinic moieties [4]. However, some smectogenic molecules can be organized differently in the smectic layers. For example, asymmetric polar molecules, such as 4-*n*-octyloxy-4-cyanobiphenyl (8OCB), present smectic A phases of period larger than the molecular length. In mixtures involving such molecules as one component, the period of the layer spacing is neither a simple function of the concentration nor of the temperature [5]. Some information regarding the molecular organization can be derived from measurement of the lattice spacing.

New smectogenic molecules have recently been synthesized for which two long aliphatic chains are grafted at each end of a rod-like core. When the number of carbon atoms in the chains varies between seven and ten, a nematic-smectic C polymorphism is obtained [6]. Increasing the chain length to over ten carbon atoms induces columnar mesophases corresponding to a decrease of the core order parameter. It is therefore of interest to measure the apparent molecular length in such mesophases and to follow the influence of different kinds of rod-like molecules upon the organization of the mixtures.

2. Phase diagrams

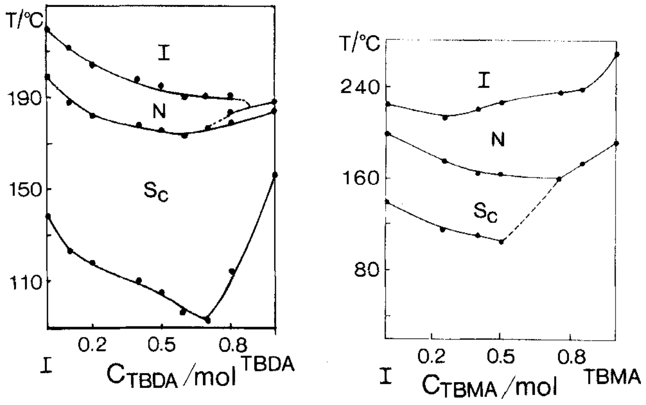
The biforked mesogen studied in this work is formulated as:



(I)

with the sequence: C 138°C S_C 199·5°C N 223·5°C I, [7]. In order to have a concordant temperature range of the mesophase for this component of the binary mixture, rod-like compounds belonging to the terephtal bis-alkylanine series were chosen. The decyl homologue (TBDA) [8] has S_A and S_C phases in addition to other ordered smectics (I, F, G); the shortest homologue: terephtal bis methylaniline (TBMA) [9], which is only nematic between 150 and 240°C, offers the opportunity to test the role of the cores.

After a first survey of the phase diagram with optical observation of contact preparations, we established the high temperature part with D.T.A. analysis performed on a Mettler TA apparatus; the temperature scanning rate was 5°C/min. The phase diagrams are shown in figure 1, and the temperatures correspond to the average of those obtained from the heating and cooling curves. We have focused our attention upon only the nematic and smectic C phases; the zone of S_F and S_I is not well established. In any case, large biphasic regions appear at the boundary between the ordered and fluid mesophases. The biforked compound 'I' is totally miscible with the nematic phase of TBMA and with the smectic C phase of TBDA, but the transition temperatures at each boundary do not depend linearly on the concentration. The binary diagram I-TBDA has a N-SmA-SmC triple point.



(a) (b)

Figure 1. (a) Phase diagram for the I-TBDA system. (b) Phase diagram for the I-TBMA system.

3. X-ray diffraction experiments

We have performed the majority of our experiments on aligned samples. The samples were contained in Lindemann glass tubes, and these tubes were placed in an oven between the poles of a magnet with the magnetic field perpendicular to the capillary tube axis. The X-ray beam was obtained from a double bent graphite monochromator and the diffraction pattern was recorded on flat or on cylindrical photographic film. In fact, two different apparatuses and magnets were used. A permanent magnet with a 0·3 T field produces good alignment of the nematic phase, but it is not always sufficient for the study of the smectic phases. Using this set-up, the temperature can be maintained to within ±0·25 K. An electromagnet giving a 1·7 T field yields good alignment of the smectic A and C phases, but the temperature control is not as good (± 1 K). Powder patterns performed with a Guinier camera give us the lattice spacing of the smectic phases with good accuracy.

At about 210°C, the X-ray diffraction pattern of compound I shows a nematic phase with a smectic C phase at a lower temperature: two broad crescents at large angle with a maximum of intensity in a reciprocal plane perpendicular to the director and four rather sharp, diffuse spots lying at a small angle of diffraction. These spots come from smectic C fluctuations (these are commonly known as skewed cybotactic groups) [10] with a finite correlation length in the nematic phase. The apparent molecular length can be deduced from the measurement of the component of the scattering vector parallel to the director. The angle between this scattering vector and the director is equal to the angle between the director and the normal to the pseudo-smectic C planes. In addition to these usual features, a few lines perpendicular to the director are also detected. They are equally spaced and correspond therefore to periodic columns of molecules, and the periodicity in these columns parallel to the director (42 Å) is different from the length of molecules in an extended comformation (51 Å), while the apparent length of molecules in the smectic C fluctuations is nearly equal to that length. Therefore, two different periods coexist along the director even in the pure compound. Moreover, these diffuse lines are also seen in the diffraction patterns of I-TBMA mixtures that are rich in compound I. They decrease with increasing concentration in TBMA and disappear for a concentration of TBMA > 75 per cent. With a larger amount of TBMA, the diffuse lines reappear but the period of the corresponding column is equal to the length of a TBMA molecule. Similar observations have been made in other nematics [11]. In contrast, in mixtures of I-TBDA, the diffuse lines remain visible without a change in the period for concentrations of TBDA $\leqslant$ 60 per cent (see figure 2). Polydomain samples of smectic C with a unique molecular orientation can be obtained by cooling these samples in the smectic C phase in a high magnetic field. The tilt angle can be estimated from the lattice spacing of the smectic C phase, assuming that the apparent length of the average molecule in a given mixture is independent of the temperature and can be deduced from the nematic or smectic A phase. This angle decreases slowly with the concentration of TBDA and with increasing temperature (see figure 3).

In a low magnetic field, a different diffraction pattern in the smectic C phase for both I-TBDA and I-TBMA mixtures is obtained. With a large amount of compound I, this pattern has a low symmetry. The observation of Bragg reflections seems to indicate a diffraction pattern of a unique, single domain of smectic C phase (see figure 4). The layer planes are nearly parallel to the capillary axis, perpendicular to the magnetic field. The high angle diffuse ring no longer has a mirror symmetry and is composed of two parts: the most intense component corresponds to molecules or

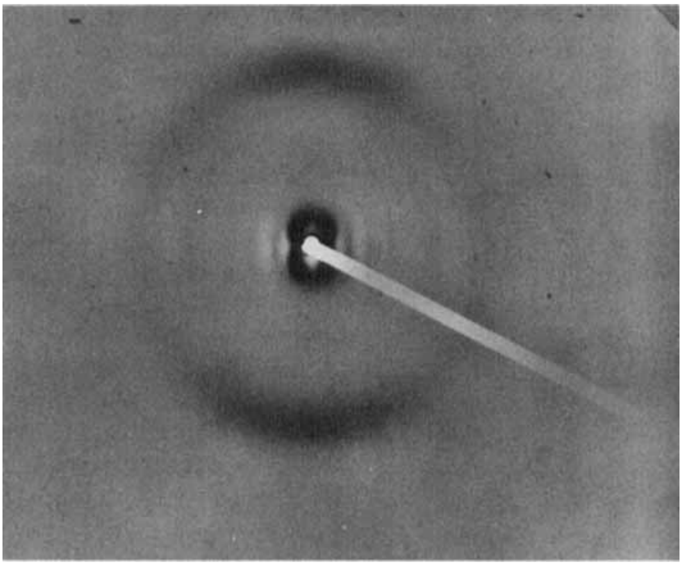


Figure 2. X-ray diffraction pattern of the nematic phase of a sample with 25 per cent TBDA and 75 per cent I, oriented in a 0·3 T magnetic field. Monochromatic CuKα radiation was used.

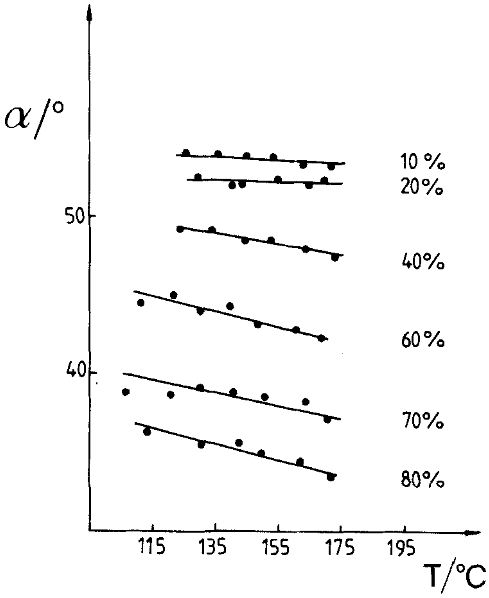


Figure 3. The temperature dependence of the tilt angles of I-TBDA mixtures in the S_C phase. The concentrations indicated are in the molar percentage of TBDA.

parts of molecules that are elongated in a direction making an angle of about 45° with the normal to the smectic plane while the less intense part corresponds to objects that are elongated along the normal to smectic planes. Such observations show that estimates of the molecular length and the tilt angle are not obvious in the smectic C phase. For samples rich in TBDA, the diffuse spots characteristic of smectic C

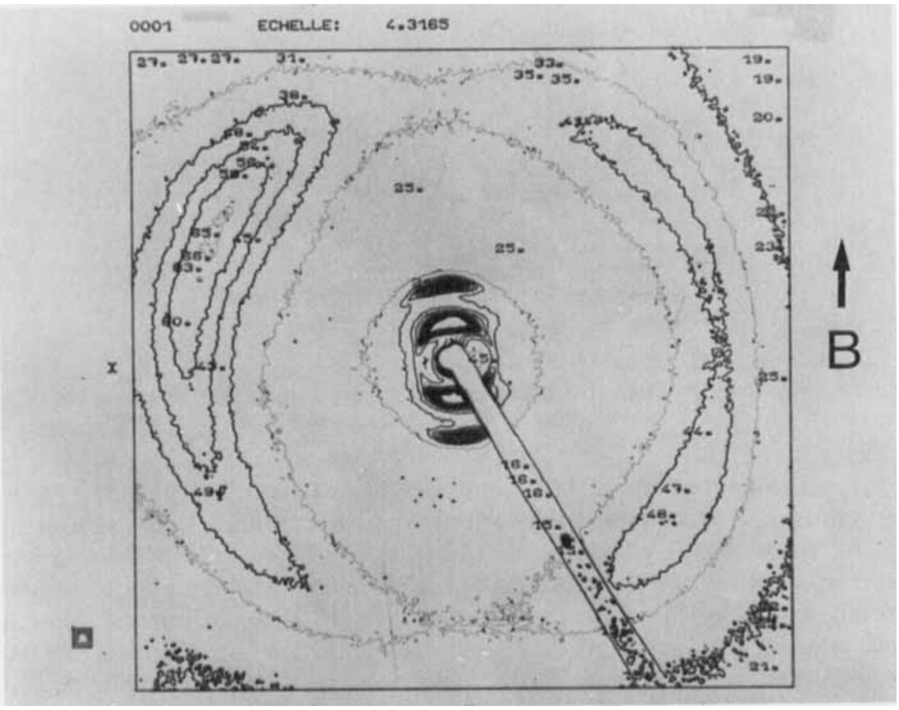


Figure 4. The microdensitometrical representation of a S_C diffraction pattern of a sample with 25 per cent TBMA and 75 per cent I. The sample is oriented in a 0·3 T magnetic field.

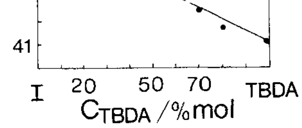


Figure 5. The concentration dependence of the apparent molecular length in the nematic phase of I-TBMA mixtures.

fluctuations lie on the meridian parallel to the director in the nematic phase. This is due to the vicinity of the smectic A phase. The apparent molecular length can therefore be deduced directly from the small angle diffuse spots. Figure 5 shows the dependence of the apparent molecular length of the smectic fluctuations in the nematic phase on the concentration of I-TBDA mixtures. For high concentrations of I, this length follows the Vegard law. When the amount of TBDA is more than 60 per cent, the points lie on a straight line $(1 - C_2)L_1' + C_2L_2$ where L_2 and C_2 are the

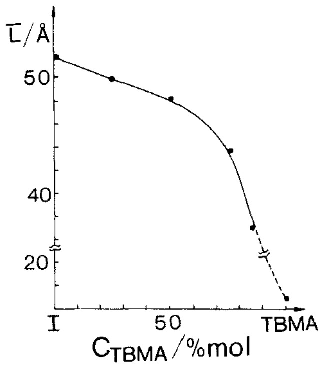


Figure 6. The concentration dependence of the apparent molecular length in the nematic phase of I-TBDA mixtures.

length and concentrations of TBDA molecules and L_1' is smaller than the apparent length of I(51 Å) and is close to the period inside the molecular columns seen in the nematic phase of pure compound I. The transition between the two linear curves occurs in a narrow composition range near 60 per cent. In figure 6, we report the apparent molecular length in the nematic phase of I-TBMA mixtures. For high concentrations of I, this length decreases slowly with increasing amounts of TBMA, and the decrease in the length becomes more and more important. For large concentrations of TBMA, the slope of the curve is very high.

4. Discussion

Let us first consider the I-TBMA mixtues. In pure compound I in the nematic phase, the majority of molecules are organized in small domains of smectic C fluctuation. It is likely that the core density is low in order to allow a close packing of the chains in pseudo-smectic layers. The first TBMA molecules can fill the aromatic layer without affecting the chain packing. Assuming that the core layer has a length (along the director) of $C_1L_1a + C_2L_2a$, where L_1a and L_2a are respectively the core length of compound I and TBMA, the apparent length of the mixtures will follow the linear law:

$$L = L_{ch} + C_1L_1a + C_2L_2a,$$

where L_{ch} is the chain length (which is constant). Our experimental data fits such a law for C_2 up to 50 per cent. If we add more TBMA molecules, the packing of the cores is denser than that of the chains, and therefore the chain layer decreases in thickness. Since TBMA molecules are very short compared to compound I, the smectic C fluctuations also disappear progressively, and mainly longitudinal correlations are found in pure TBMA. Looking at the diffraction pattern of pure compound I, it is obvious that in addition to smectic C fluctuations, columns of molecules are aligned along the field direction. These molecules have a different conformation, since the period in the columns is smaller than for the smectic fluctuations. These columns are still present in the smectic C phase at high temperature, consequently, the diffraction pattern of the smectic C phase for samples rich in compound I is consistent with the idea that a small fraction of molecules of compound I are in a zig-zag conformation with the longest dimension of 46 Å (see figure 7). For mixtures with TBDA, the idea

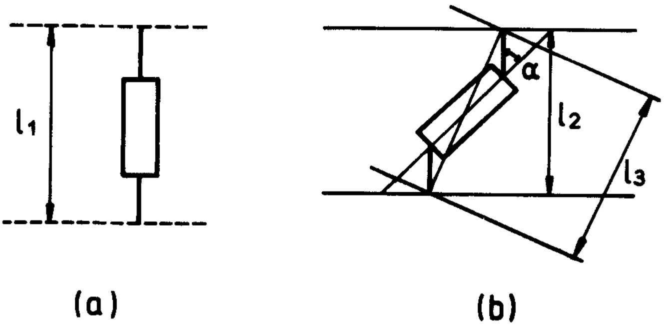


Figure 7. Schematic representation of elongated and zig-zag conformations of the mesogens. For compound I, we have (*a*) $L_1 = 51{\cdot}1$ Å is the molecular length in an elongated conformation measured from molecular models and found from the S_C fluctuations in the nematic phase of both samples rich in compound I and in pure compound I (*b*) zig-zag conformation with $L_2 = 42$ Å, $L_3 = 46$ Å, $\alpha = 45°$. L_2 is approximated to the longitudinal correlation periodicity in the nematic phase of either pure compound I or samples rich in I, L_3 is the apparent molecular length of I in mixtures rich in TBDA, α is the angle between the chain orientation and the long axis of the core.

of a zig-zag conformation is also favoured by the existence of two regimes in the dependence of the apparent molecular length versus concentration. We note that the transition between the two regimes occurs at a concentration of TBDA of about 65 per cent, i.e. near the triple point in the phase diagram, this point divides the phase diagram into two parts where the properties of compound I and TBDA dominate, respectively. For mixtures with less than 60% mol in TBDA, molecules of compound I have, on majority, an extended conformation, and the slope of the curve in figure 5 accords with Vegard's law. In contrast, for mixtures rich in TBDA, the curve has a smaller slope, and the apparent molecular length corresponds to a Vegard law with molecules of compound I in their zig-zag conformation with a length of 46 ± 2 Å. Let us remark that the previous discussion assumes that the molecular cross section perpendicular to the director is equal for the two species. If we try to explain the discrepancy from the simple Vegard law as due to a larger molecular cross section for compound I than for TBDA, then the apparent molecular length versus I/TBDA concentration curve would differ by a smaller slope for low TBDA concentrations and a greater slope for high concentrations than the Vegard law. This is, in fact, the opposite effect from what is observed. However, we do not have enough information to establish a more sophisticated model. A knowledge of the specific gravity and of the birefringence would be helpful to gain a better insight into the molecular organization.

Nevertheless, our X-ray measurements, which require only a small amount of each mixture, have yielded qualitative information which can be summarized as follows: the nematic and smectic C phases of biforked mesogens are totally miscible with that of rod-like molecules. Two kinds of conformers can coexist in the mesophases of biforked molecules, and the addition of a rod-like molecule can disturb the equilibrium between these two conformers. The addition of a molecule with short paraffinic chains (TBMA) induces a better compactness of the core layer, as would be expected intuitively. These experiments are therefore a starting point for the study of other binary mixtures involving biforked mesogens.

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