Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Dbrowski, R. , Janik, J. A. , Janik, J. M. and Otnes, K.(1988) 'A neutron scattering study of dimerization and pairing of molecules in liquid crystal mixtures', Liquid Crystals, 3: 4, 443 — 452
To link to this Article: DOI: 10.1080/02678298808086393
URL: http://dx.doi.org/10.1080/02678298808086393

LIQUID CRYSTALS, 1988, VOL. 3, NO. 4, 443–452

A neutron scattering study of dimerization and pairing of molecules in liquid crystal mixtures

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(*Received 23 April 1987; accepted 3 November 1987*)

Neutron quasielastic scattering has been used to study molecular reorientation in pure 4-ethyl-4′-*n*-pentylazoxybenzene (EPAB), 4′-*n*-pentyl-4-cyanobiphenyl (5CB), 4-(trans-4′-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT) and in EPAB–5CB and EPAB–6CHBT mixtures. 5CB exhibits a much narrower quasielastic component than EPAB. We interpret this as an indication of 5CB dimerization, which causes steric hindrance to reorientation. The equimolar mixture of EPAB–5CB exhibits a significantly broader quasielastic component than that evaluated from additive contributions of the pure constituents. We interpret this as a result of complexing of 5CB and EPAB molecules, after destruction of 5CB dimers. The complex pairs DM DM DM . . . probably form immediately a DMDMDM . . . smectic layer in which individual pairs cannot be distinguished, and in which the steric hindrance to reorientation is no longer present. This picture is supported by measurements at other concentrations of EPAB and 5CB. The EPAB–6CHBT mixtures, on the other hand, show a much more additive behaviour of the constituents.

1. Introduction

It is well known that mixing polar nematics with non-polar (or weakly polar) ones leads to an induction of a smectic phase [1–4]. The highest stability of this induced smectic phase occurs for nearly equal concentrations of both constituents. Many physical properties of such mixtures (for example temperatures and enthalpies of phase transitions, elastic constants, dielectric constants and molar volumes) change non-additively with concentration [5–7]. These properties are explained by the occurrence of complex formation between the molecules of two different constituents of the mixture and destruction of the pairs of the polar component (cyanocompound) [9–11]. Usually one of the constituents of the mixture has the character of an acceptor (A) and the other that of a donor (D), since the charge transfer mechanism is at least partly responsible for this complex formation [4, 12, 13]; but other explanations have also been suggested [1, 14].

Compounds with an induced smectic phase may be divided into two main groups: in the first there are acceptor compounds with terminal CN, NO_2 or COH, they are considered by many authors as having a tendency to form dimers [8, 9, 15–18]; in some of these compounds a dynamic equilibrium between dimer and monomer strongly favours the right side of the equation

$$2A \rightleftharpoons A_2.$$

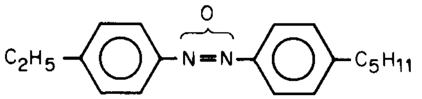
In the dimer the molecules are associated with each other via the sides of their cores, whereas their dipole moments are arranged antiparallel. Consequently the dimer has a greater length than that of the monomer; in most cases $l_{\mathrm{dimer}}/l_{\mathrm{monomer}} \sim 1{\cdot}4$. It has to be noted that this dimer structure has been questioned by some authors [19] who suggested head-to-head association. In the second group there are acceptor compounds with terminal I, Br, Cl, F, $COCH_3$ or NCS. Their molecules have no tendency to form dimers [18, 20], or perhaps only a very small one. Molecules with donor properties do not form dimers at all [21].

The induced smectic phase (for both groups of acceptors) has always a characteristic thickness of the smectic layer which is the average value of the lengths of individual acceptor and donor molecules. This indicates that, when dimer forming acceptors interact with donors, the dimers are removed according to

$$A_2 + D \rightleftharpoons AD + A.$$

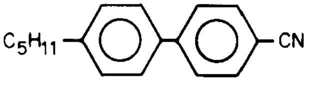
The aim of this work was to investigate the effect of molecular phenomena occurring in liquid crystal mixtures on the incoherent quasielastic neutron scattering. In the mixtures under investigation one constituent (the donor) is a weakly polar compound EPAB (4-ethyl-4′-*n*-pentyl-azoxybenzene) [22], and the other constituent (the acceptor) is, in one case, a polar compound 5CB (4-*n*-pentyl-4′-cyanobiphenyl) often considered as partially dimerized and, in the other case, it is a polar compound 6CHBT i.e. 4-(trans-4′-*n*-hexyl-cyclohexyl) isothiocyanatobenzene [23] considered as non-dimerized. The structural formulae of the corresponding molecules are

EPAB:



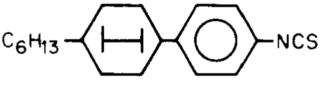
(D)

5CB:



(A)

6CHPB:



(A)

In 5CB–EPAB and 6CHBT–EPAB mixtures the induced smectic A phase occurs in the concentration range for EPAB of ~0·3–~0·8. Both mixtures have almost identical phase diagrams; figure 1 shows such a diagram for the 5CB–EPAB mixture [5]. In both cases the maximum stability of the nematic and smectic phases occurs at approximately equimolar constitution. This almost identical behaviour may stimulate some astonishment because evidently the occurrence of dimerization in 5CB, if true, has a negligible effect on the acceptor–donor pair formation (AD). Therefore, we might expect that the 5CB dimers, if they exist, will have a very small effect on the

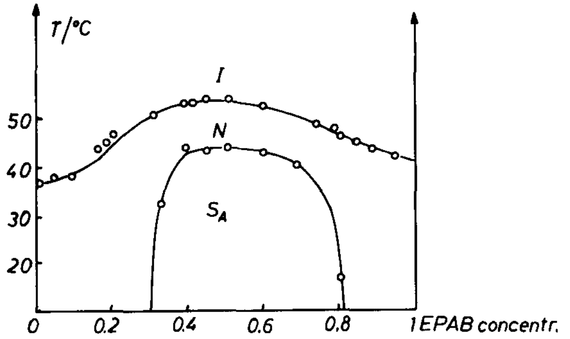


Figure 1. Phase diagram for the 5CB–EPAB mixtures.

neutron scattering pattern, whereas the AD pairs, as well defined molecular units, will influence the neutron pattern significantly. The results however indicate the opposite.

This paper claims that in pure 5CB, dimers exist as well-defined molecular units, whereas in the mixture, the AD pairs although present cannot be distinguished in the smectic layer as individuals. This favours the ADADAD . . . structure of this layer rather than the AD AD AD . . . one. In order to justify these claims it is necessary to present a basic connection between incoherent neutron scattering and molecular properties. Such a summary is given in the next section.

2. Incoherent neutron scattering and molecular properties

We emphasize here the so-called quasielastic neutron scattering (QNS) which takes place when stochastic reorientations occur. Since the hydrogen incoherent neutron scattering cross-section dominates strongly over other atoms, reorientations in which hydrogen participates are only of importance here. These reorientations are responsible for giving a quasi-elastic component around the elastic line, in the neutron scattering pattern; in the text both the quasielastic and elastic components will be denoted by QNS. Besides the elastic and quasielastic components there is also an inelastic one; in most cases it is possible to subtract this inelastic component in a natural way and thus consider only the isolated quasielastic plus elastic scattering pattern. It has to be noted here that the subtraction of the inelastic background inevitably leads to some errors. In fact these errors dominate the error bars in figure 7.

From the widths of the quasielastic components the time characteristics for reorientation can be deduced; from the ratio of elastic to quasielastic components some information concerning the reorientational model can be obtained. In both these attempts use is normally made of scattering measurements at various angles, i.e. at various neutron momentum transfers.

It is very important to remember that the QNS method can provide results only within some reorientational correlation time window. This window depends on the energy resolution of the neutron spectrometer applied; for most of the spectrometers the window is from *c.* 10^{-12} to *c.* 10^{-10} s; for some special spectrometers it can be extended by one order of magnitude towards slower motions. Thus, the QNS method must be treated as a detector of fast reorientational motions only. The lack of a quasielastic component in the neutron scattering pattern does not mean that the reorientational motions are not present, but only (strictly speaking) that their characteristic time is outside the window, which in practice means that the motions are too slow to be detected by QNS.

The QNS method has been applied successfully by various authors to liquid crystals in various phases (see, for instance, [24–26]). Only reorientations of molecules around their long axes happened to be fast enough to be detected via the existence of a quasielastic component. Various model interpretations were proposed for the motions in question. Convincing arguments exist [26, 27] that the dominating role is played by the intramolecular reorientational motion of two moieties consisting of the benzene rings coupled with the aliphatic chains. This intramolecular motion, while relatively free in the liquid crystal phases, is in most cases (although not always [28]) stopped (or at least considerably slowed down) below the melting point, certainly via intermolecular hindrance. It is essential to note here that the moieties motion is not affected by the nematic–smectic transition, thus the QNS patterns below and above this transition look very similar.

3. Results and discussion

Figure 2 presents a comparison of incoherent, quasielastic neutron scattering spectra (QNS) measured at room temperature for pure EPAB and pure 5CB. The spectrometer resolution function is also shown. Figure 3 shows a similar comparison for pure EPAB and pure 6CHBT. These spectra were obtained at the time-of-flight spectrometer TOF installed at the cold neutron source of the JEEP II reactor of the

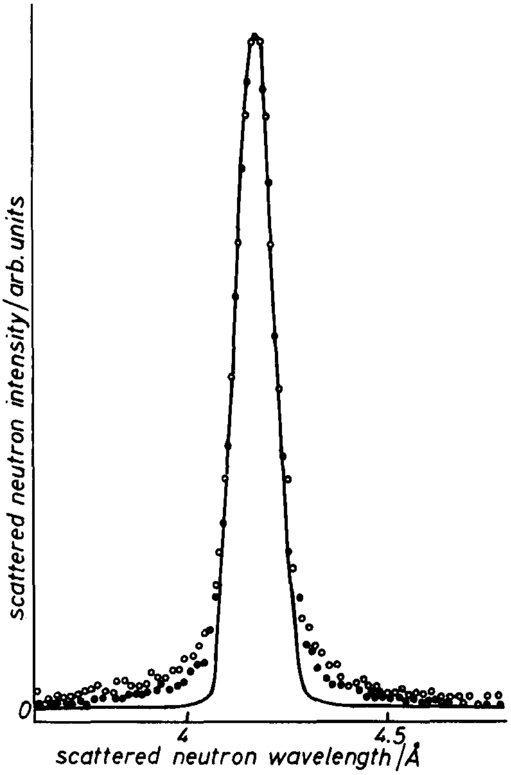


Figure 2. Spectra of neutrons incoherently, quasielastically scattered by pure EPAB (○) and pure 5CB (●). The solid line represents the spectrometer resolution. Measurements were made at room temperature for a scattering angle of 40°. The background of inelastically scattered neutrons was subtracted as a smooth line.

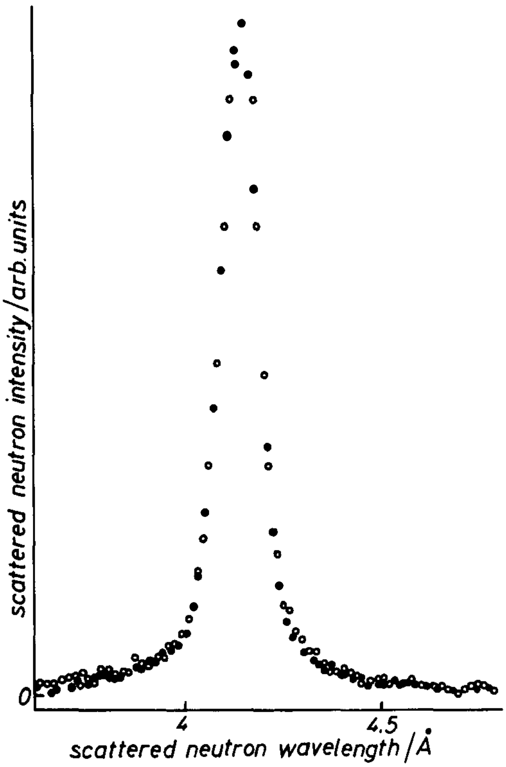


Figure 3. Spectra of neutrons incoherently, quasielastically scattered by pure EPAB (○) and pure 6CHBT (●). Measurements were made at room temperature for a scattering angle of 40°. The background of inelastically scattered neutrons was subtracted as a smooth line.

Institutt for energiteknikk, Kjeller, Norway. All of these spectra are results of a procedure of subtraction of a smooth background of inelastically scattered neutrons. Since this paper does not make use of any models for molecular motion the angular dependence was not exploited and the measurements correspond to only one scattering angle, namely 40°.

We can see that although all of the spectra show quasielastic components (wings), these components are more pronounced for both EPAB and 6CHBT than for 5CB. As a matter of fact, when comparing 5CB not only with EPAB and 6CHBT but also with other liquid crystals which were studied in our laboratory, it turns out that the 5CB pattern has an exceptionally unpronounced QNS component. We suggest that this relative reduction of the QNS component in 5CB is evidence for dimer formation, which leads to steric hindrance to reorientations of the moieties in molecules, around the single bond connecting the benzene rings. Figure 4 illustrates the fact that the rotational properties in a 5CB dimer are no doubt quite different from those in a monomer.

Figure 5 presents the QNS spectrum obtained at room temperature for the 5CB–EPAB mixture, with an EPAB concentration of 0·5. This spectrum is compared with that calculated from the pure 5CB and the pure EPAB spectra (of figure 2) by using the additivity assumption; this has to be understood in the following way. We assume that in pure 5CB and pure EPAB the scattering units are hydrogen atoms,

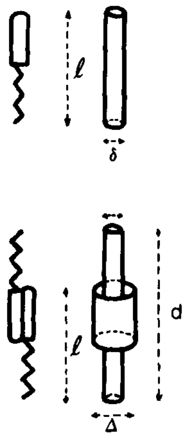
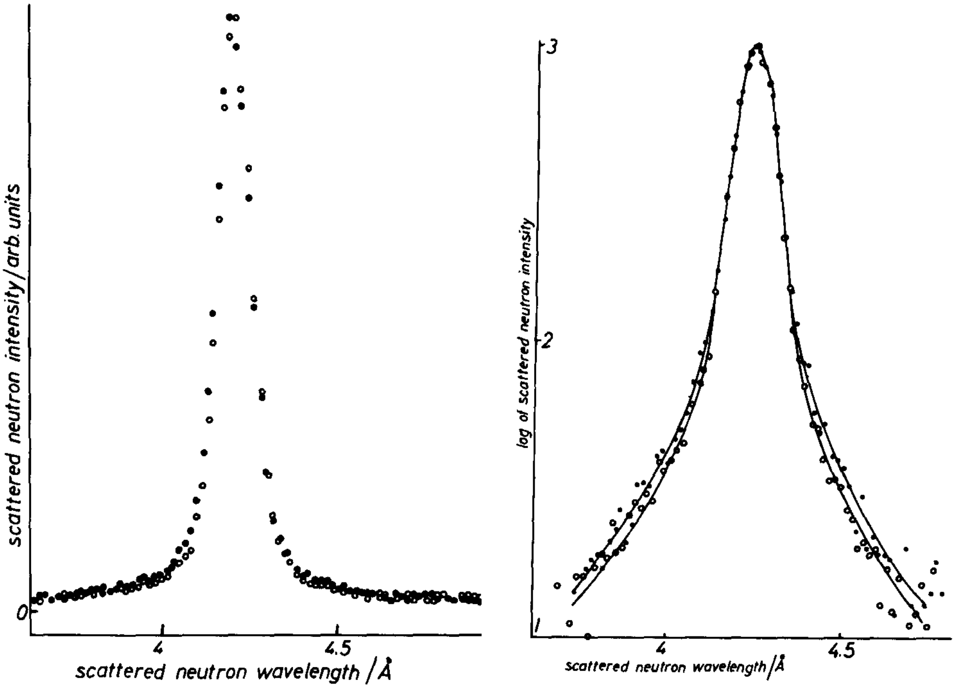


Figure 4. Schematic representations of the 5CB monomer and dimer.



(*a*) (*b*)

Figure 5. (*a*) Spectrum of neutrons incoherently, quasielastically scattered by the 5CB–EPAB mixture with a concentration of 50 per cent EPAB (●). Measurements were made at room temperature with a scattering angle of 40°. The background of inelastically scattered neutrons was subtracted as a smooth line. Open circles (○) correspond to a spectrum calculated from pure 5CB and pure EPAB spectra (of figure 2) with the assumption that hydrogen atoms of the pure constituents contribute to the scattering proportionally to their concentration in the mixture. (*b*) The same in the logarithmic scale of the vertical axis. The curves are only guides to the eye through the points.

which participate in the spectrum of the mixture proportionally. The comparison reveals a disagreement, the spectrum measured experimentally has a broader QNS component than that given by the assumption of additivity. We suggest this is a result of the fact that, in the mixture of this concentration, practically all of the 5CB dimers

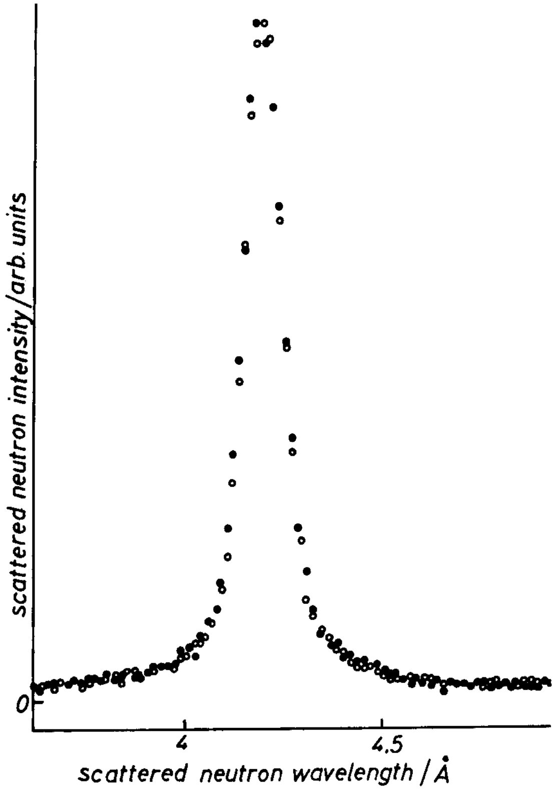


Figure 6. Spectrum of neutrons incoherently, quasielastically scattered by the 6CHBT–EPAB mixture with a concentration of 50 per cent EPAB (●). Measurements were made at room temperature for a scattering angle of 40°. The background of inelastically scattered neutrons was subtracted as a smooth line. Open circles (○) correspond to a spectrum calculated from pure 6CHBT and pure EPAB spectra (of figure 3) with the assumption that hydrogen atoms of the pure constituents contribute to the scattering proportionally to their concentration in the mixture.

(whose hydrogen atoms were hindered in their reorientations) are destroyed and replaced by 5CB–EPAB pairs. In these 5CB–EPAB pairs the steric hindrance for reorientation of the moieties is evidently much smaller than in 5CB dimers. In fact the measured spectrum of the mixture does not differ from all other known QNS spectra of nematic and/or smectic A phases, whereas the pure 5CB spectrum differs from those considerably.

We are not undermining here the well-established fact of pair formation in the mixtures. We only claim that the non-additivity illustrated in figure 5 provides an additional argument (to figure 2) for 5CB dimer formation in pure 5CB and, moreover, provides an argument that in the 5CB–EPAB pairs steric conditions are such that reorientations are still possible. Perhaps this is due to the fact that the pairs AD AD AD . . . immediately form an ADADAD . . . layer of the induced smectic A phase, in which the individual pairs cannot be distinguished [29]. In other words the short range ordering is dominated by the long range one.

This conclusion is corroborated by the results obtained for the 6CHBT–EPAB mixture (see figure 6). The results are in this case much closer to an additive composition (in the sense explained previously) of the results for the pure constituents.

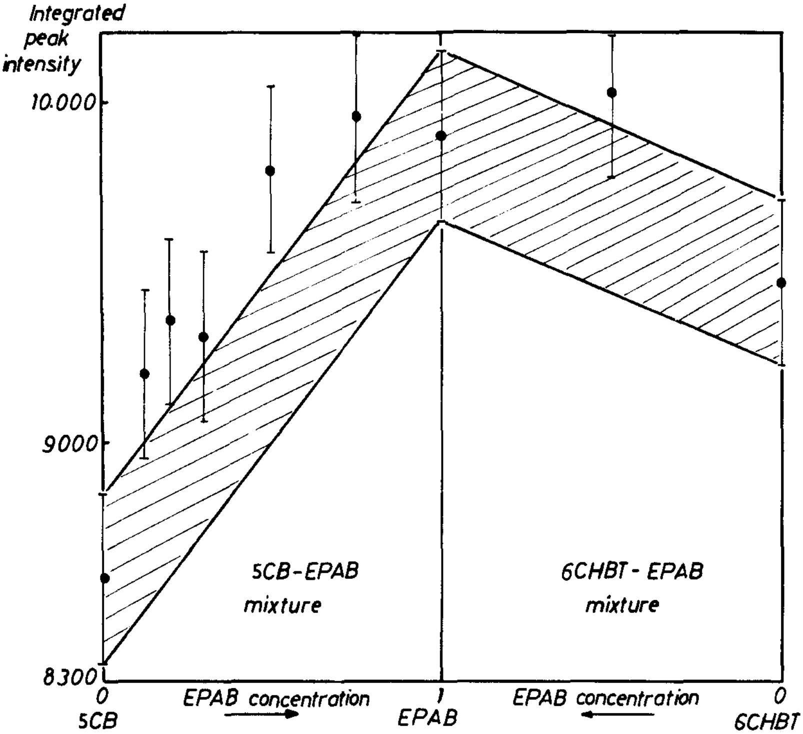


Figure 7. Integrated results of quasielastic neutron scattering (QNS) in 5CB–EPAB and 6CHBT–EPAB mixtures at various concentrations. Points (●) are experimental. Error bars are mostly due to errors in the inelastic background evaluation. The shadowed areas represent the region when the additivity assumption is valid, when the error bars of the pure constituents are taken into account.

This reduces the role of dimer formation in pure 6CHBT and, at the same time, shows that in 6CHBT–EPAB pairs there is not much hindrance for the reorientation of the molecular moieties. Thus, the heterocomplexes so formed are very weak. Indeed this result is consistent with those of a dielectric study [30].

Figure 7 shows the QNS results for all of the concentrations investigated in a representation different from that in the previous figures. We simply make use of the fact that the integral over a broader spectrum has a larger value than that over a narrower one, when both spectra are normalized to the same peak value. Such integral values are compared in figure 7 with the additivity assumption. We can clearly see that the additivity assumption does not explain the experimental results for 5CB–EPAB mixtures.

4. Conclusion

The smectic A phase created by pairing of 5CB and EPAB molecules scatters neutrons in practically an identical way as the uncoupled EPAB molecules. Since the incoherent, quasielastic neutron scattering is sensitive to reorientations of the molecular moieties (approximately around the long axis), we conclude that the situations of the EPAB molecules before pairing and after the formation of the induced smectic phase via pairing are similar, in the sense that the steric hindrance to reorientation is in an induced smectic A similar to that in normal smectic A or nematic phases. Hence the pairing does not lead to a creation of any additional barrier to reorientation. This may indicate that in the induced smectic A phase the layer situation is rather of the DMDMDM . . . type than of the DM DM DM . . . type.

Quite a different situation exists for 5CB. A significantly narrower quasielastic component indicates that the dimerization process strongly influences the reorientations. Moreover, the individual dimers must not have too short a life time ($> 10^{-10}$ s) in order to be observed by neutrons as individual units.

Our thanks are due to Dr. Patricia Cladis from the A.T. and T. Bell Laboratories and to Professor Dietrich Demus from the Sektion Chemie of the Martin Luther University in Halle for helpful discussions.

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