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A complementary structural study of 4-*n*-nonyl-4″-cyanoterphenyl

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A complete structural study of several homologous alkylcyanoterphenyls has been presented by Leadbetter *et al.* We draw here a comparison between this study and our own work for 4-*n*-nonyl-4″-cyanoterphenyl. Essentially we confirm the main results obtained by Leadbetter *et al.* but an additional E″ phase has also been studied by optical microscopy and X-ray diffraction. This phase with E symmetry but with a monolayer character hampers the study of the E′ phase and may prevent the observation of a devil's staircase in this system.

1. Introduction

Highly polar substituents, e.g. CN or NO_2, are often incorporated into liquid crystal compounds to allow them to be oriented through electric field poling. These substituents, however, induce new correlations, essentially of a dipolar nature between molecules and favour an antiparallel arrangement of the permanent dipoles. At different temperatures, the relative strengths of the dipolar and steric interactions change which results in the appearance of a quite complex polymorphism [1–3]. On the other hand, cyano substituted mesomorphic side chain polymers have shown promising potentialities in the field of optical display devices and of non-linear optics [4–6]. In order to understand the intermolecular forces which control the mesomorphic organization in such systems, we have studied the monomeric model compound, 4-*n*-nonyl-4″-cyanoterphenyl (9CT) by DSC, optical microscopy and X-ray diffraction.

Meanwhile Professor A. J. Leadbetter and his colleagues had also, independently, been studying the homologous series of which our model compound is a member. Since their study was completed before ours and because they kindly sent us a reprint of their manuscript [7], we shall in this short paper only point out the similarities in results and a few differences in the approach. In the following, we shall extensively use the notation adopted by Leadbetter *et al.* in their paper.

2. Comparison between our results and those of Leadbetter *et al.* [7]

This comparison will only focus on 9CT which is the only compound of the series that we have studied. We confirm the transition temperatures measured by Leadbetter *et al.* through DSC and textural observations. However, we have been able to observe the texture of the additional phase detected by Leadbetter *et al.* in the DSC trace between the E′ and S_{Ad} phases. In the following, we shall call this additional phase E″, by extending the notation of Leadbetter *et al.*

2.1. *Optical microscopy*

Figures 1–8 present the mesomorphic textures of compound 9CT observed under a polarizing microscope (Olympus BHA-P) on samples sandwiched between coverslips and heated on a Mettler hot stage. On cooling from the isotropic state, the high temperature mesophase appeared at 210°C as a schlieren texture (see figure 1). From the observation of disinclinations of strength $\pm\frac{1}{2}$ this mesophase was identified unambiguously as a nematic phase [8]. Further decrease in temperature produced a focal conic fan texture (see figure 2) consistent with a S_A phase. When cooled to 116°C the focal conic fans of the S_A phase became crossed with concentric arcs running across the backs of the fans (see figure 3). The arcs were not transitory in nature but were permanent, thus indicating the existence of a E phase, referred to as E″. At the E″–E′ transition, the paramorphotic arced focal conic fan texture persisted on the whole (see figure 4), but colour changes occurred at the E′–E transition with the pink–yellow E′ conics becoming more yellow in the E phase (see figure 5).

This material also showed a strong homeotropic tendency in all liquid-crystalline phases. The homeotropic texture exhibited by the S_A phase appeared black with oily streaks starting from air bubbles. Upon cooling the S_A dark homeotropic texture in the E″ phase, a black, grey and white platelet texture formed (see figure 6). The platelets overlap one another and are crisply outlined. Upon cooling to the E′ phase there were only slight differences (see figure 7). Upon passing to the E phase, however, the platelets disappeared to give rise to an ill-defined texture (see figure 8).

2.2. *X-ray diffraction experiments*

Our X-ray diffraction patterns are similar to those obtained by Leadbetter *et al.* [7]. and have mostly been recorded on equivalent equipment. As far as the S_{Ad} phase is concerned, we have obtained the same value for the smectic period and therefore confirm the classical molecular organization suggested by Leadbetter *et al.* [7] for this phase. However, we have detected on overexposed patterns the existence of weak S_{CI} fluctuations (usually called skewed cybotactic groups) with coherence lengths $\xi_{\parallel} \approx 50$ Å and $\xi_{\perp} \approx 30$ Å along and perpendicular to the meridian, respectively. This situation is comparable to that already found in the S_{Ad} phase of 8COOCB [9].

We also agree with the cell dimensions given by Leadbetter *et al.* [7] for the E phase. These dimensions lead to a reasonable value for the density of this phase. We would just mention that the small difference of about 3 Å between the layer spacing c of 30·5 Å and the molecular length L of 27·5 Å is comparable to the mean thermal displacement of the molecules along the director in the solid-like smectic phases [10]. Therefore, though this small difference of 3 Å definitely exists, its physical interpretation in terms of overlap is unwarranted.

We could not obtain very well aligned samples of the E′ phase. In particular, we could not determine the detailed diffraction patterns in the 20 l, 11 l and 21 l rows any better than Leadbetter *et al.* [7] and could not rule out a slight tilt angle. Nevertheless, we also observed the commensurate lock-in of the two density waves ($q_1 = \frac{3}{4}q_2$ with $q_1 \approx 2\pi/35$ Å^{-1} and $q_2 \approx 2\pi/26$ Å^{-1}) which results in the appearance of a superstructure with period c of 104 ± 1 Å for the compound 9CT. The experimental intensities of the 00 l reflections could also be accounted for by essentially the same type of model

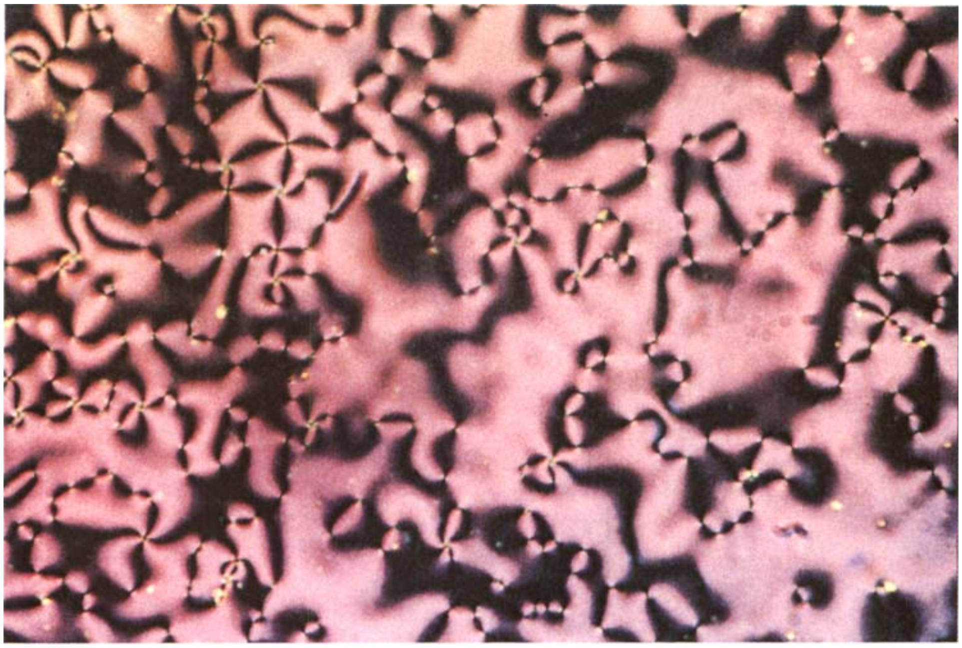


Figure 1. The schlieren texture of the nematic phase of 9CT at 207·8°C. Crossed polarizers. Magnification 200 ×.

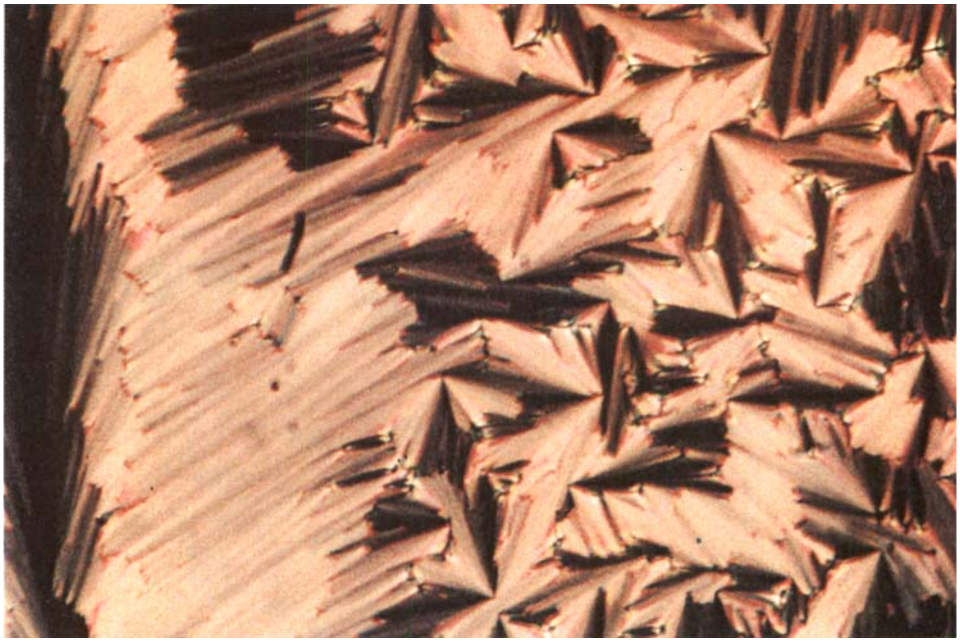


Figure 2. The focal conic fan texture of the S_A phase of 9CT at 117°C. Crossed polarizers. Magnification 200 ×.

Figure 3.

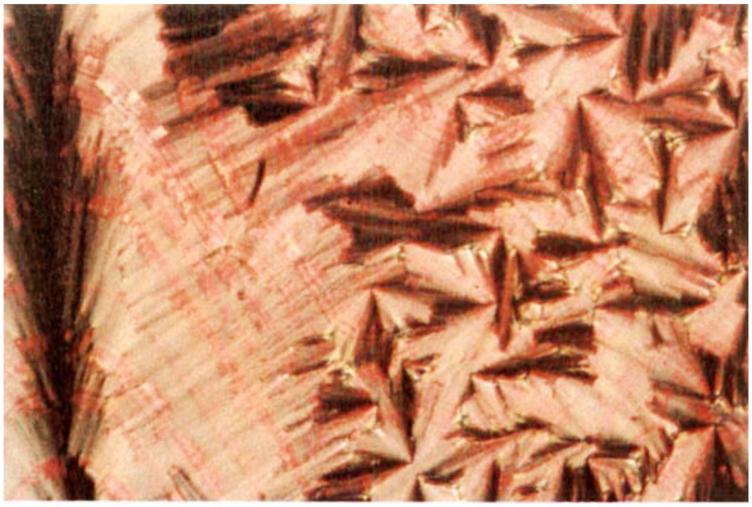


Figure 4.

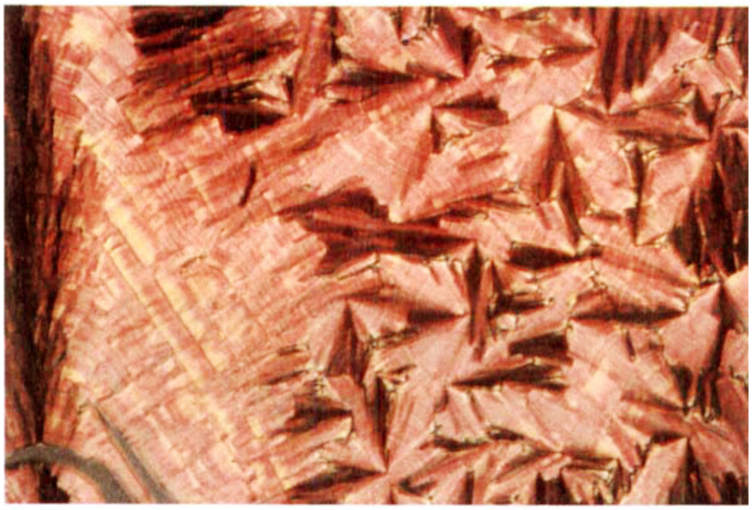
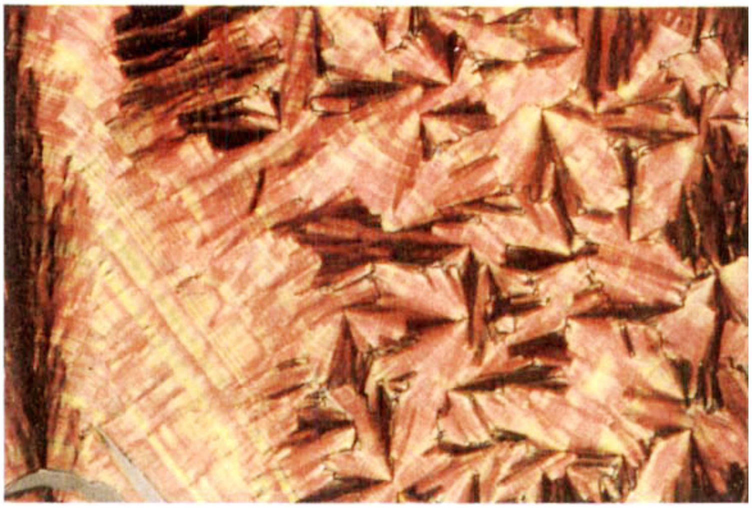


Figure 5.



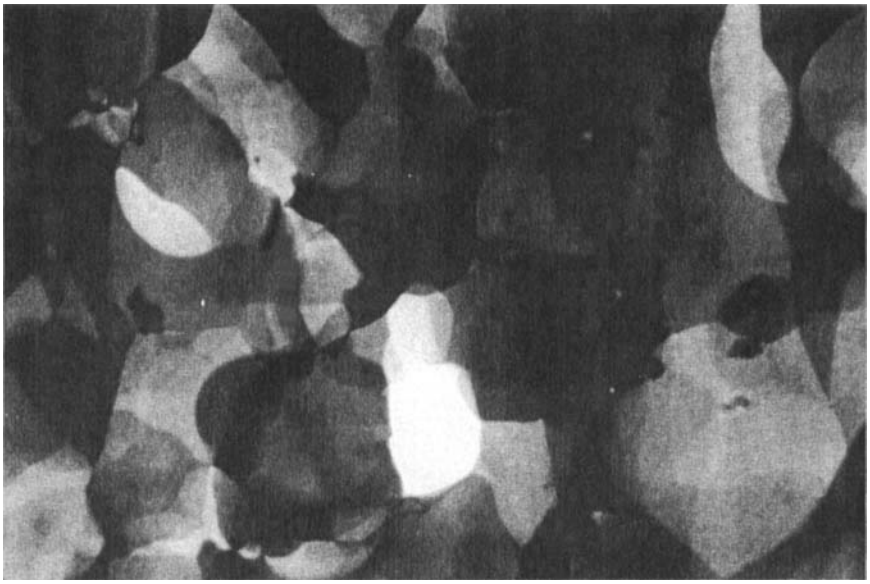


Figure 6. The texture obtained on formation of the E″ phase of 9CT upon cooling the homeotropic texture of the S_A phase, 115·6°C. Crossed polarizers. Magnification 200 × .

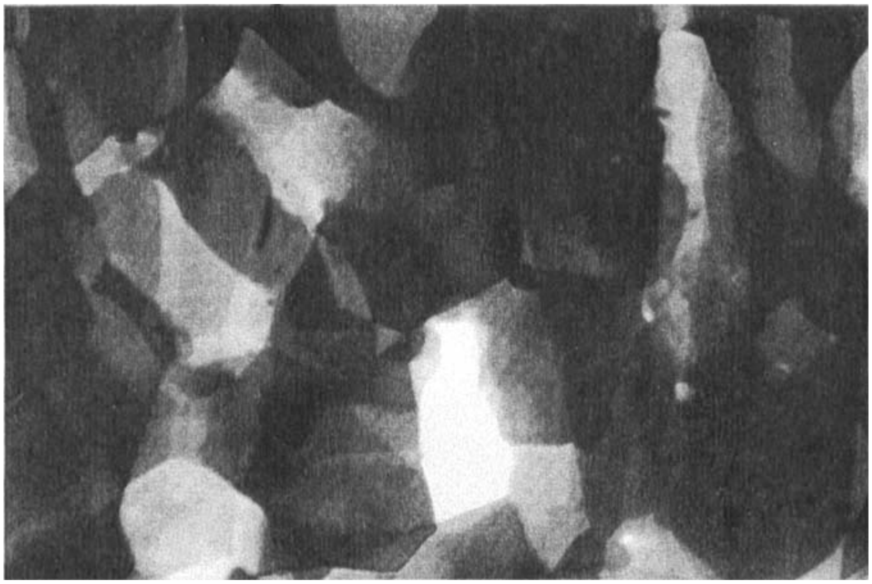


Figure 7. The platelet texture of the E′ phase of 9CT formed on cooling the texture of the E″ phase, 111·6°C. Crossed polarizers. Magnification 200 × .

Figure 3. The paramorphotic arced focal conic fan texture of the E″ phase of 9CT at 115°C. Crossed polarizers. Magnification 200 × .

Figure 4. The paramorphotic arced focal conic fan texture of the E′ phase of 9CT at 111·6°C. Crossed polarizers. Magnification 200 × .

Figure 5. The paramorphotic arced focal conic fan texture of the E phase of 9CT at 105·0°C. Cross polarizers. Magnification 200 × .

Figure 8. The texture of the E phase of 9CT formed on cooling the texture of the E′ phase, 105·1°C. Crossed polarizers. Magnification 200 ×.

as that presented by Leadbetter *et al.* [7]. We also mention that we did not find such a difference in intensity between the 002 and 004 reflections for 9CT as for 8CT: $I_{004}/I_{002} \approx 100$ for 8CT while $I_{004}/I_{002} \approx 10$ for 9CT. This might show that the packing densities of the monolayer and partially bilayer sublayers have closer values for 9CT than for 8CT.

The only really original feature of our study compared to that of Leadbetter *et al.* [7] consists in the better determination of the E″ phase. In addition to its weak DSC signal and its uneasy texture observation, this phase manifests itself by its contribution to the X-ray diffraction patterns. On heating the E′ phase to about 115°C, (see figure 9) new reflections appear on the power patterns and also on the oriented

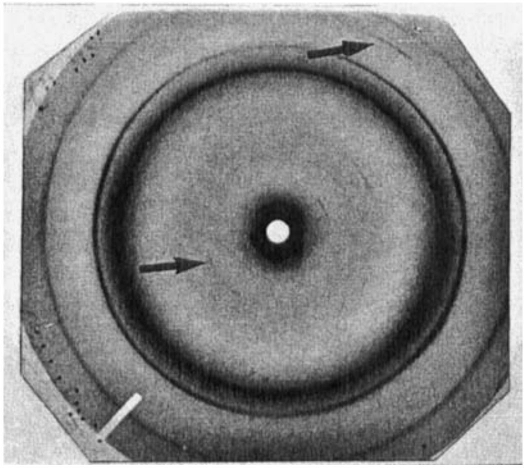


Figure 9. Powder diffraction pattern of 9CT at 115°C which shows the additional lines brought about by the E″ phase. (The arrows point to two of these lines.)

ones. Some of these reflections of appreciable intensity, are located at small angles. Some other lines are very faint and located at wide angles. Moreover their intensity decreases sharply with scattering angle which is indicative of strong thermal motions, all of these new reflections are listed in the table.

Measured and calculated lattice spacings in the E″ phase; $a = 8{\cdot}05 \pm 0{\cdot}05$ Å, $b = 5{\cdot}45 \pm 0{\cdot}05$ Å, $c = 28{\cdot}2 \pm 1$ Å.

d_{meas}/Å	*hkl*	d_{calc}/Å
*	001	28·2
14·2 ± 0·4	002	14·1
9·3 ± 0·4	003	9·4
7·10 ± 0·05	004	7·05
4·52 ± 0·01	110	4·51
4·25 ± 0·05	112	4·30
4·03 ± 0·01	200	4·02
3·85 ± 0·05	202	3·87
3·51 ± 0·05	204	3·50
3·23 ± 0·01	210	3·24
3·10 ± 0·05	212	3·16

*The 001 reflection could be observed but not measured (see text).

The E″ phase could not be obtained pure which prevents us from measuring the 001 reflection properly because it was located too close to the 004 reflection of the E′ phase on some diagrams recorded with the usual equipment or it was too weak on the diagrams recorded with a Guinier camera. Similarly, its *hk*0 reflections could not be separated from those of the E′ phase. (The *a* and *b* cell parameters for the three E, E′ and E″ phases are nearly identical.) The E″ phase is of the monolayer type and it differs from the E and E′ phases by the fact that several 00*l* reflections can be detected. This means that the electron density profile along the normal to the layers is much sharper than in the E and E′ phases. Moreover several *hkl* reflections (such as 112, 202, 204 and 212) can be seen which suggests that the interlayer correlations are stronger in this phase. All this makes the E″ phase look more ‘crystal-like’ than the E and E′ phases.

3. Discussion

Since our study essentially confirms the results obtained by Leadbetter *et al.* [7] we shall only mention a few ideas about the influence of E ordering upon the incommensurate behaviour of 9CT.

The compounds belonging to the homologous alkylcyanoterphenyl series give us the opportunity to check experimentally several points of the theory of the incommensurate smectic phases [2]. For such polar compounds, two incommensurate layer thicknesses can coexist in the system. The coupling between these two wavevectors gives rise to a polymorphism in which a periodic network of solitons parallel to the layer planes induces a modulation of the layer thickness. Therefore, a sequence going from a S_{Ad} phase to a S_{A1} phase can take the appearance of a devil's staircase. Actually, strictly infinite periodic networks of solitons have not been observed so far in liquid S_A phases. More often a modulation of the layer thickness occurs in another direction and discommensuration walls nearly perpendicular to the layer planes appear. This is the case for the two dimensional $S_{\tilde{C}}$ phase [1, 2].

An additional in-plane periodic ordering can make the establishment of a S_C phase type modulation more difficult. In fact, such discommensuration walls can coexist with an hexatic ordering, the two networks being then almost independent [11]. In a three dimensional ordered layered phase, the solitons will be of lower energy if they are parallel to the layer planes. Therefore, the E′ phase could correspond to the initial theoretical description given by Prost and Barois [2]. Then, the modulation wavevector can present a devil's staircase behaviour [12, 13] with a rather large step for $q_1/q_2 = \frac{3}{4}$ followed at higher temperature by smaller steps for $q_1/q_2 = m/n$ with large n. Within the experimental accuracy, the wavevector q_1 will seem to vary continuously in this temperature range. From this point of view the study of Leadbetter *et al.* [7] does not seem to be detailed enough in order to answer this question securely. However such an investigation is extremely difficult because of the very narrow temperature range of the E′ phase and because sometimes, by the time thermal equilibrium was reached, degradation of the sample had already started as could be seen by the change of the transition temperatures. Furthermore, at the same time, we have detected a new monolayer phase, E″, which appears slowly from the E′ phase, probably following a nucleation growth process on a long time scale. This process might also be sensitive to the presence of impurities in the samples. Though Leadbetter *et al.* [7] only detected the E″ phase on cooling the S_{Ad} one, we also observed it, by optical microscopy, on heating the E′ phase. This kind of situation has already been encountered for the compounds NH_4HSeO_4 and ND_4DSeO_4 [14] for which the study of the incommensurate phases was made difficult due to the presence of metallurgical processes creating internal stresses inside the samples and disturbing the measurements. From this respect, it is not surprising that the E behaviour is reminiscent of that of other molecular crystals but this makes the observation of a devil's staircase difficult in this system

We are greatly indebted to Professor A. J. Leadbetter for kindly sending us a preprint of his study on the same subject. We would also like to thank Drs. J. Prost and F. Dénoyer for helpful discussions. Two of the present authors are obliged to Dr. A. R. Tajbakhsh and Professor G. W. Gray for kindly placing at our disposal the compound 4-*n*-nonyl-4″-cyanoterphenyl.

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