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## Liquid Crystals

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### Unusual structures in some alkyl cyanoterphenyls

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## Unusual structures in some alkyl cyanoterphenyls

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The phase behaviour of three alkyl cyanoterphenyls has been investigated with the particular objective of elucidating their unusual phase behaviour and determining the structure of the new, and so far uncharacterized, phase (E') appearing between the smectic  $A_d$  and the crystal E phases. In the course of this work complications arose from the appearance of yet another phase which appears only on cooling but for which no characteristic X-ray diffraction pattern could be obtained. The E' phase appears to have the orthorhombic symmetry characteristic of the E phase but has a complex temperature dependent packing in the  $c$  direction. This is driven by the competition between a density wave and an antiferroelectric pair ordering which results in a locked-in structure with a periodicity of three times that of the underlying density wave.

### 1. Introduction

A large amount of previous work has been reported on the structures of the liquid crystals formed by compounds with cyano end groups [1-4]. The presence of the strong cyano dipoles gives a tendency for molecular association and results in nematic or smectic A structures with a characteristic periodicity or pseudo-periodicity ( $L'$  = layer spacing) along the director considerably greater than the molecular length ( $L$ ). For a wide range of compounds the characteristic length  $L'$  is close to that of a molecular (aromatic) core and two tails [2] and it is now generally accepted that this partial bilayer ( $S_{A_d}$ ) structure is based on an overlapping, through antiferroelectric association, of the molecular cores imposed upon the normal tendency (in orthogonal smectic liquid crystal phases) for the periodicity to be close to the molecular length ( $L$ ). The possible results of this competition between the two order parameters represented by the length scales  $L$  (monomer) and  $L'$  (pair) have been considered by Prost [5] in connection with investigations of re-entrant phase behaviour, transitions from monolayers to bilayers and an earlier report [2] of structures with incommensurate, coexisting density waves in alkyl cyanoterphenyls. Prost has shown that the coupling between the two order parameters is able, in principle, to account for all of these behaviours.

The earlier results [2] on the terphenyls showed clearly, over a very wide temperature range, the presence in the nematic phase of 4- $n$ -pentyl-4''-cyano- $p$ -terphenyl

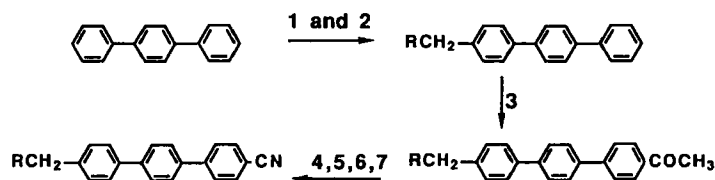
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(5CT) of two coexisting colinear damped density waves of wavelengths  $L$  and  $L'$  as defined here. A similar behaviour, but with periodicities  $L'$  and  $2L$ , has also been found more recently in the  $S_A$  phase of a mixture of two compounds [6]. The behaviour of 4-*n*-octyl-4''-cyano-*p*-terphenyl (8CT) was normal in the nematic and  $S_A$  phases showing the presence of a single partial bilayer ( $L'$ ) density wave. On cooling into the disordered crystal E phase however, a very complex behaviour was found, involving independent coexisting density waves, longitudinal modulations, and a normal E phase successively appearing with decreasing temperature.

The purpose of the work reported in this paper was to investigate the unusual phase behaviour and structures in 8CT in more detail and to extend the experiments to neighbouring *n*-CTs which show similar behaviour. In order to facilitate discussion the phase(s) intermediate between the  $S_A$  and E phases are designated as  $E'$  since they appear to have the same symmetry as the normal E phase [7].

## 2. Experimental

The preparation of the compounds will be described more fully in a subsequent publication. The synthetic scheme is however shown here. The final products were purified by column chromatography (silica gel) using chloroform/light petroleum (b.p. 40–60°C) as eluant. All spectral data were consistent with the required structures and analytical HPLC gave purities of 99.9 per cent. With appropriate deuteriated starting material and reagents, the scheme was also used to prepare fully deuteriated 4-*n*-nonyl-4''-cyano-*p*-terphenyl (9CT). Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC 2C with data station, and optical microscopy was carried out using an Olympus BPSP 753 polarizing microscope in conjunction with a Mettler MP5 hot stage and control unit.



1,  $RCOCl/AlCl_3/CH_2Cl_2$ ; 2,  $LiAlH_4/1:1, CHCl_3:Et_2O$ ; 3,  $CH_3COCl/AlCl_3/CH_2Cl_2$ ; 4,  $NaOBr/dioxan$ ; 5, thionyl chloride; 6, aqueous  $NH_4OH$ ; 7, thionyl chloride/dimethylformamide.

Synthetic scheme.

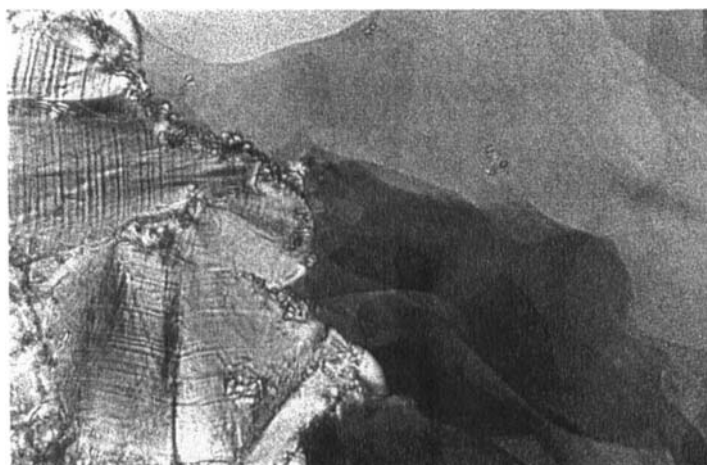
X-ray diffraction studies were carried out using 1 mm thick samples sandwiched between aluminium foil windows as an integral part of an aluminium block. Temperature control was to  $\pm 0.2^\circ C$ . Alignment of nematic phases was achieved by holding the sample in a 0.15 T magnetic field during the experiment. Fibre alignment of smectic phases was achieved by cooling from the isotropic liquid to the smectic A phase in a field of 1.7 T at rates of around  $1^\circ h^{-1}$ , followed by removal from the field. Diffraction patterns were recorded using flat-plate X-ray film (Kodak no-screen) or a multiwire proportional counter [8]. Some samples examined using the proportional counter were mounted on a 4-circle goniometer to facilitate optimization of the alignment for a given domain. Features close to the origin of reciprocal space (see later) were recorded with a 1.6 m long helium filled flight tube between the (fixed) sample and the detector.

### 3. Results

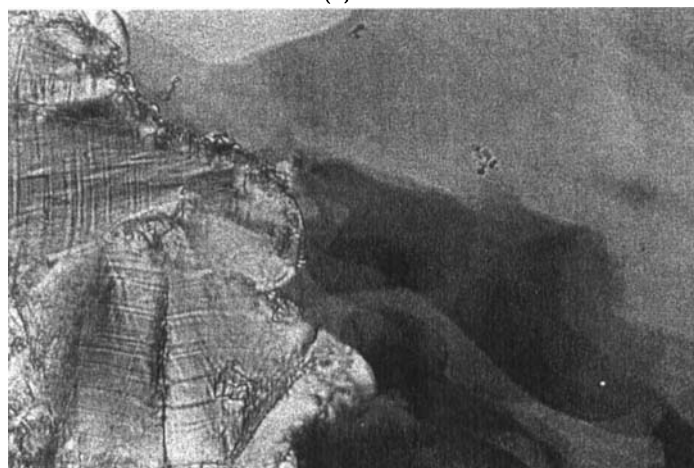
#### 3.1. Phase behaviour

For all three compounds, a very unusual phase behaviour is observed as determined by DSC, optical microscopy and X-ray diffraction. On heating, the crystal melts to give an E phase which transforms, dependent on chain length, in the range 106 to 120°C to a new phase (E') with a range of existence varying from 2° for 8CT to 8° for 10CT. This transforms to a normal  $S_{A_d}$  (partial bilayer) phase [7] and the two lower homologues also show a nematic phase before melting to the isotropic liquid at over 200°C.

A miscibility diagram of state showing clearly that the lower temperature E phase of 9CT is miscible with a classical E phase, and that the E' phase is distinct from either an E or a B phase has been published [9]. Table 1 summarizes the results for DSC and optical microscopy. Figure 1 shows photomicrographs of the E and E' phases of 9CT.



(a)



(b)

Figure 1. Photomicrographs ( $\times 100$ ) of the (a) E and (b) E' phases of 9CT. The bands on the fans of the classified E phase are more clearly defined. At the E-E' transition there is a change in the shape and definition of the platelet areas.

Table 1. Transition temperatures and enthalpies of transition from differential scanning calorimetry. Transition temperature ranges from microscopic studies are given in parentheses.

	Crystal 1	→	Crystal 2	↔	E	↔	8CT	E'	↔	smectic A	↔	nematic	↔	liquid
$T/^\circ\text{C}$	79.8 (77)		85.8 (86)		118.9 (117-117.6)		121.1 (119-120.1)		197.0 (197.4-197.9)		213.0 (213.3-213.9)			
$\Delta H/\text{kJ mol}^{-1}$		←	16.33	→	2.07		3.46		0.18		0.95			
	Crystal	↔	E	↔	E'	↔	9CT	smectic A	↔	nematic	↔	liquid		
$T/^\circ\text{C}$	85.1 (87.4)		110.9 (109.8-110.3)		117.1 (117.5-118.3)		205.0 (205.3-205.8)		210.6 (211.4-211.7)					
$\Delta H/\text{kJ mol}^{-1}$	20.19		1.74		3.27		0.51		1.00					
	Crystal 1	↔	Crystal 2	↔	E	↔	10CT	E'	↔	smectic A	↔	liquid		
$T/^\circ\text{C}$	77.7		86.2 (87.2)		108.0 (107.5-108.0)		116.2 (116.7-117.6)		205.0 (204.8-205.9)					
$\Delta H/\text{kJ mol}^{-1}$		←	28.52	→	1.53		3.24		4.15					

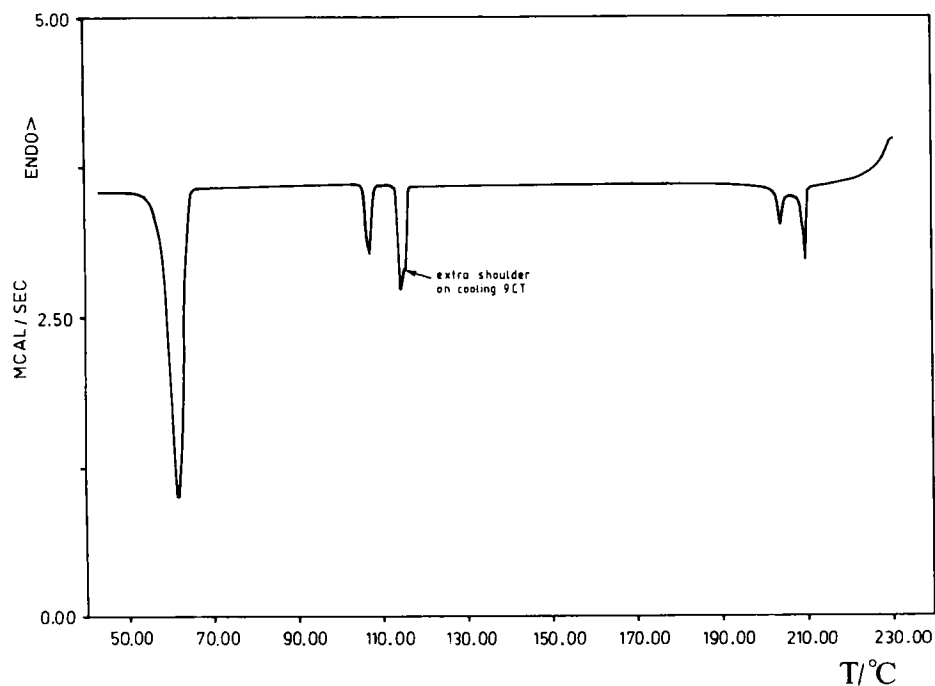


Figure 2. Typical DSC data obtained on cooling 9CT; scan rate  $-10.00^{\circ}\text{C min}^{-1}$ .

On cooling 10CT, DSC reveals an additional phase between the A and E' phases. In 8CT and 9CT, a small additional peak appears in the DSC traces on cooling, but now this is on the high temperature side of the larger, higher temperature peak of the (E  $\rightarrow$  E'  $\rightarrow$  S<sub>A<sub>d</sub></sub>) doublet. The separation from the large S<sub>A</sub>  $\rightarrow$  E' peak is only about 1°C. For perdeuteriated 9CT, the small additional transition is more clearly separated (by about 5°C) from the doublet, while for 10CT the additional, poorly resolved peak appears between the two peaks of the doublet. A typical DSC trace obtained on cooling 9CT is shown in figure 2, the extra shoulder is clearly visible. The DSC cooling trace for deuteriated 9CT has already been published [9]. What is happening is clearly that an additional phase appears on cooling by virtue of a supercooling of the S<sub>A</sub>  $\rightarrow$  E'  $\rightarrow$  E transitions.

### 3.2. X-ray diffraction

The diffraction patterns of the nematic phases of 8CT and 9CT aligned in a 0.15 T field show normal behaviour with no evidence for the two coexisting damped density waves found in 5CT [2]. The S<sub>A<sub>d</sub></sub> phases of all three compounds also show normal behaviour with good alignment and only a very weak, second order layer reflection (see figure 3). The phase in all cases is of type S<sub>A<sub>d</sub></sub> with a layer spacing close to the length of the aromatic core plus two tails. The temperature dependence of the layer spacings is shown in figure 4 and numerical results are given in table 2.

The E phases exhibit a typical diffraction pattern for that phase showing 00 $l$ , 20 $l$ , 11 $l$ , 21 $l$  reflections whose widths are resolution limited. In fact, even for 00 $l$  the reflections for  $l > 1$  are very weak ( $I(002)/I(001) < 0.01$ ) showing that the layers are very soft even though the phase is clearly crystalline. The orthorhombic unit cell dimensions are given in table 3 and the marked decrease in layer spacing from the S<sub>A<sub>d</sub></sub>

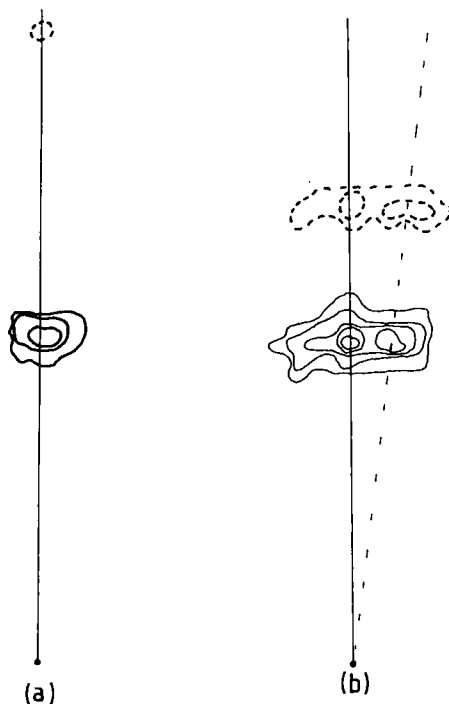


Figure 3. Typical diffraction patterns along  $00l$  for aligned specimens of (a)  $S_{A_d}$  and (b)  $E'$  phases.

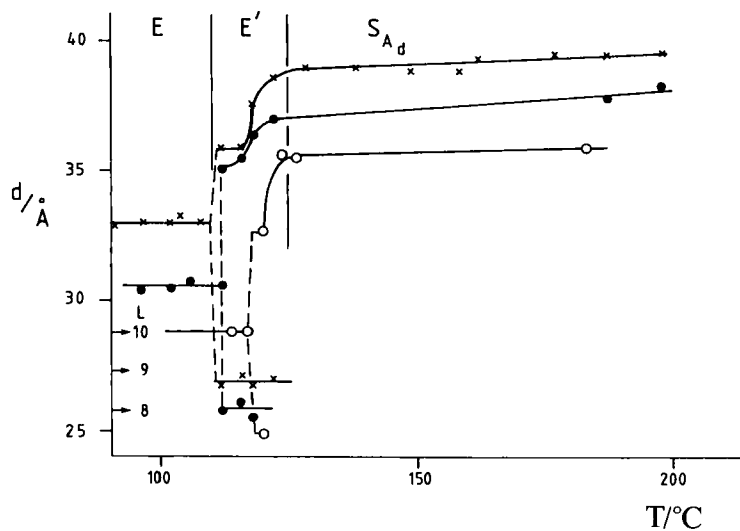


Figure 4. Plots of layer spacings for 8CT, 9CT and 10CT showing the phase changes from  $S_{A_d}$  to  $E'$  to  $E$  compared with molecular lengths. The lines are guides to the eye.

phase is shown in figure 4. The layer spacing is, however, significantly greater than the molecular length and still corresponds to a form of partial bilayer structure.

The single additional phase observed between the  $E$  and  $S_{A_d}$  phases on heating has a clearly recognizable diffraction pattern characterized by the strongest  $00l$  reflection

Table 2.  
(a) Measured layer spacings.

	$S_{Ad}$		$E'$		$E$		Molecular length/ $\text{\AA}$	
8CT	$T/^\circ\text{C}$	183	126.5	124	120	117	114	25.8
	$d/\text{\AA}$	35.9	35.6	35.7	32.7	28.8	28.9	
					24.9			
9CT	$T/^\circ\text{C}$	197.5	187	122	118	115.5	112	27.3
	$d/\text{\AA}$	38.3	37.8	37.0	36.4	35.5	35.0	
					25.5	26.1	25.8	
10CT	$T/^\circ\text{C}$	198	187	177	162	158.5	149	28.8
	$d/\text{\AA}$	39.6	39.5	39.5	39.3	38.8	38.9	
					38.6	37.6	35.9	
					27.0	26.8	27.2	26.8

Accuracy of data approximately 1 per cent.

(b) Lock-in  $q$  values ( $q = 2\pi/d$ ).

	10CT	9CT	8CT
$q_2/\text{\AA}^{-1}$	0.233	0.242	0.252
$q_1/\text{\AA}^{-1}$	0.175	0.179	0.192
$\Delta q = q_0/\text{\AA}^{-1}$	0.058	0.063	0.060
8CT	$q_{\text{obs}}/q_1 = 0.33, 0.66, 1.00, 1.33, (1.66), 1.98, 2.33$		



located between those of  $S_{A_d}$  and E (see figures 3 and 4) together with a second, weaker  $00l$  reflection at a scattering vector corresponding to a layer spacing about  $1 \text{ \AA}$  less than the molecular length, i.e. a monolayer spacing.

The wider angle diffraction pattern is very similar to that for the E phase but because very good sample alignment could not be obtained (see later and figure 3) the detailed diffraction patterns as a function of  $l$  in the  $20l$ ,  $11l$  and  $21l$  rows could not be determined. The intensity profiles suggest that the phase still has orthorhombic symmetry but a tilted phase with a tilt angle of less than approximately  $5^\circ$  cannot be ruled out. The aligned  $E'$  phase was obtained by cooling from the  $S_{A_d}$  phase but a number of domains was always found with a mosaic spread of up to  $10^\circ$  despite starting from a very well aligned  $S_{A_d}$  (see figure 3 and 5). Nevertheless there was usually a major domain so that reasonably accurate intensity measurements were possible and weak reflections detectable.

Despite many attempts, including experiments kindly carried out by Dr. J. M. Seddon at the University of Southampton using a continuously scanning Guinier camera, no additional change of diffraction pattern was observed on cooling which could be associated with the extra phase transition found in the DSC measurements.

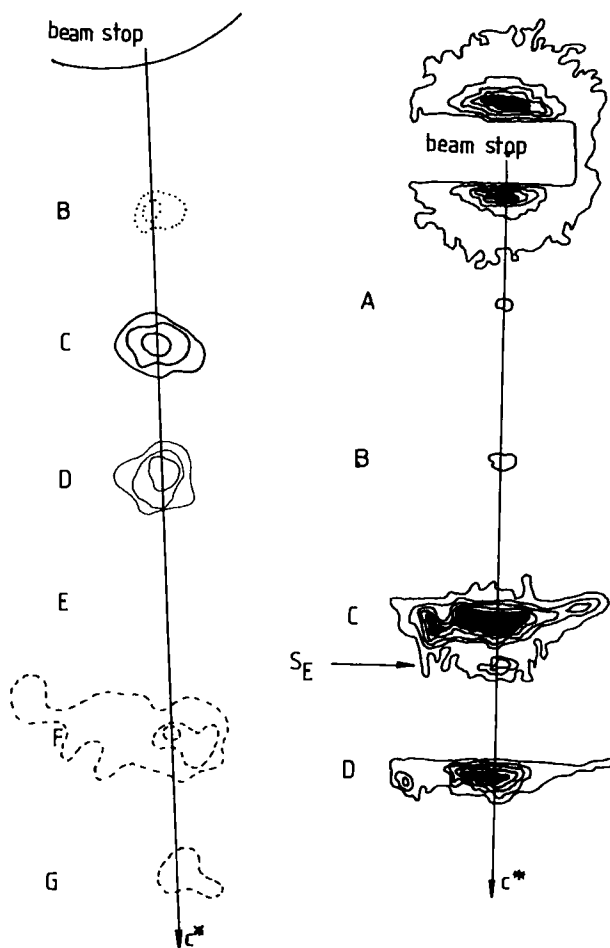


Figure 5. Intensity data along  $00l$  for 8CT in the  $E'$  phase, A to G label the  $00l$  reflections in the locked-in configurations from  $q/q_0 = 1$  to 7.

Table 3. Orthorhombic cell dimensions for the E phases.

	8CT	9CT	10CT
$a/\text{\AA}$	7.98	7.92	8.00
$b/\text{\AA}$	5.52	5.53	5.48
$c/\text{\AA}$	28.8	30.6	33.0

Table 4. Measured relative intensities of 00 $l$  reflections for 8CT in the E' phase.

$q/q_0$	1	2	3	4	5	6	7
I	12(6)	27(7)	10 <sup>d</sup>	2180(200)	5(5)	45(10)	7(3)

Estimated uncertainties in parentheses are derived from the spread of values in different experiments.

The results obtained were indistinguishable on heating and cooling. This extra phase transition is undoubtedly real but since it is revealed as an undercooling phenomenon it could be sample and experiment dependent and, in any case, any structural change associated with it must be very small.

More detailed study of the E' phases of all three compounds showed first the presence of a number of additional weak spots along 00 $l$  and secondly a significant temperature dependence of the position of the strongest 00 $l$  reflection but not of the weaker (monolayer) reflection. These results are given in table 2 and in figure 4 and the intensity data are given for 8CT in table 4. These are not very accurate because of the mosaic spread and the weakness of most of the reflections, but they were obtained by averaging data obtained with different exposure time, collimation and sample rotation about an axis perpendicular to  $c$ . The most extensive results were obtained for 8CT but the relative intensities are very similar for the other compounds.

The results may be summarized as follows. At the transition from  $S_A$  to E' the density wavevector  $q_1$  decreases to a smaller value and a second 00 $l$  diffraction spot appears at a wavevector  $q_2 \approx 4q_1/3$  with an intensity about 20 per cent of the  $q_1$  spot, together with other very much weaker 00 $l$  reflections. Within experimental error  $q_2$  is independent of temperature while  $q_1$  increases with decreasing temperature and appears to lock-in at a value  $q_1 = (3/4)q_2$  (see table 4). For 8CT the whole array of 00 $l$  reflections was measured and the values are also given in table 4; they form a regular periodic array with  $\Delta q = q_1/3$ .

### 3.3. Comparison with earlier X-ray results on 8CT

The present results show very similar behaviour for all three compounds and this is significantly different from earlier 8CT data which appeared to show a change from a modulated structure to two incommensurate density waves with change of temperature [2]. It required many experiments to understand these differences. For some earlier specimens there is a very wide coexistence range so that the E phase may coexist with the  $S_{A_d}$  phase, with both E' and  $S_{A_d}$  and with E' alone. This occurs on both heating and cooling and is particularly noticeable for perdeuterated 9CT, but the effect was not found in the later batches of fully hydrogenous materials where only the usual very small coexistence of adjacent phases was observed. The 9CT did contain  $c$ . 1.8 per cent of protons through exchange during the synthesis, and the earlier batches of 8CT were made by a less efficient route, whereby the  $-\text{CONH}_2$

group was introduced into the 4-alkyl-*p*-terphenyl by reaction with oxalyl chloride followed by ammonolysis. The scheme now used certainly allowed more ready purification of intermediates and final products. It is possible, therefore, that the observed differences are purity related, although this was not revealed spectroscopically or otherwise in the earlier materials.

#### 4. Discussion

The highly unusual structural changes described here may be understood qualitatively in terms of the competition between two order parameters: the density wave and the antiferroelectric ordering, with characteristic lengths  $L$  and  $L'$  respectively, as discussed by Prost [5]. In the  $S_{A_d}$  phase the antiferroelectric order parameter dominates so that the density modulation is based on the natural pair length  $L'$ . On cooling, a first order transition occurs to an E-type phase, probably having orthorhombic symmetry in which first an incommensurably modulated structure is obtained which is essentially a superposition of two independent density waves:  $q_2 = 2\pi/L$  and  $q_1(T) \approx 2\pi/L'$  where  $L' > L$  is determined by the antiferroelectric order parameter.  $q_1(T)$  then locks in at a value  $q_1 = (3/4)q_2$  to give a simple periodic behaviour characterized by a wavevector  $q_0 = q_1/3$ . There is then a second, first order transition which leads to a normal crystal E-phase with a simple layer periodicity locked-in at a new value intermediate between  $q_1$  and  $q_2$  and larger also than  $q_1$  for the  $S_{A_d}$  phase. A full theoretical description incorporating the two first order phase changes as well as a subtle interplay of the two order parameters will be far from simple to achieve.

The question of the molecular configuration in the E' phase which has a periodicity  $q_0$  approximately four times the molecular length is best addressed by a Fourier synthesis along the layer normal ( $z$ ). The data in table 3 show that there are only two Fourier components of significant weight ( $3q_0$  and  $4q_0$ ), hence making the assumption of a centrosymmetric structure, the electron density is given by

$$\rho(z)/\rho_0 = \pm 100 \cos 6\pi z \pm 47 \cos 8\pi z,$$

where  $\rho_0$  is an unknown normalization factor. Incorporation of the remaining Fourier components would have only very minor effects on the result. The uncertainty in the signs of the two components is in fact of no importance because the different combinations merely change the position of the origin along  $z$  or the sign of the electron density.

The result is shown in figure 6 which represents all the information directly obtainable from the diffraction data. Thus the structure, while certainly periodic, is soft, that is the layers are relatively weak and disordered. Figure 6 shows the oscillation about the average of the electron density along  $z$ . Relative values of the electron density averaged over the whole molecule and for the core (plus CN) and alkyl tail are readily obtained and are respectively 7.4, 8.6 and 5.4. Hence by associating electron density maxima and minima with regions comprising predominantly molecular cores and tails, it is clear that tails must be located in the regions where the electron density is furthest from the average value. A schematic picture of a possible molecular arrangement in the E' phase can thus be deduced and is also shown in figure 6. This clearly illustrates the way in which the locked-in compromise between the molecular density wave and antiferroelectric order parameters is realized. It must be emphasized that the molecular positions shown in figure 6 are only schematic, there is considerable disorder and the molecular positions cannot be located precisely.

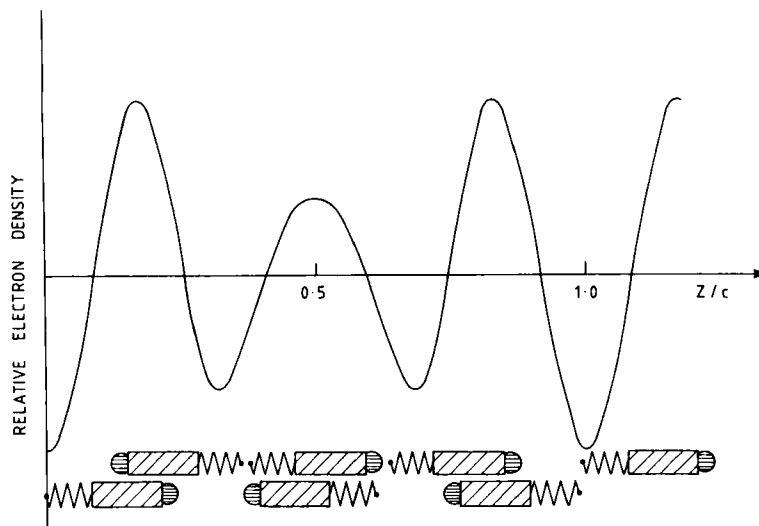


Figure 6. The relative electron density along the  $c$  direction from Fourier synthesis of the experimental data. The probable average molecular packing is also shown.

The remaining problem in these materials is to investigate more carefully the actual transition region between  $S_{A_d}$  and  $E'$  phases, where there could perhaps be an additional modulated phase, and in any case to establish the precise nature of the temperature dependence of the structural modulations and more information about the three dimensional aspects of the molecular arrangement in the  $E'$  phase.

Finally it is interesting to contrast the effects discussed here with a different type of behaviour found in a number of liquid crystal compounds [10–13] in which crystal B phases show a variety of long wavelength ( $c. 100 \text{ \AA}$ ) transverse modulations of the layers with the wavevector of the modulation parallel to the layers and the molecular displacements normal to them. These modulated structures appear to arise also as a result of a competition between the density wave and an order parameter associated with local packing of the molecules. In these cases, however, it appears that this order parameter is associated with space filling requirements, rather than a dipolar interaction, leading to relative longitudinal displacements of lateral neighbours like that found in the tilted phases observed at lower temperatures, and resulting in the observed transverse modulations.

We acknowledge financial support from the SERC and thank Dr. J. M. Seddon (University of Southampton) for additional X-ray measurements in support of our search for the still uncharacterized extra phase. These measurements were however useful in confirming the phase behaviour reported herein.

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