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X-ray diffraction studies on *cis*- and *trans*-4'-cyanobiphenyl-4-yl 3-*n*-propylcyclobutane-1-carboxylate

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X-ray diffraction has been used to study the nematic phases of the *cis* and *trans* isomers of an elongated molecule containing the cyclobutane group. It has been shown that these nematic phases consist of a mixture of single molecules and overlapping core dimers. It has been found that increasing the temperature of the *cis* isomer rapidly reduces the dimer population, whereas increasing the temperature of the *trans* isomer enhances the dimer population. This provides an explanation of the relatively high clearing temperature of the *trans* isomer. The different temperature dependences of the dimer population in the *cis* and *trans* isomers has been explained by a model involving inversion of the cyclobutane group.

1. Introduction

Recently we have published [1] work on the synthesis and physical properties of compounds of structure (I), incorporating the cyclobutane, spiro(3.3)heptane or dispiro(3.1.3.1) decane rings.



R = alkyl



Y = alkyl or cyano.

During this work, successful separation, by HPLC, was achieved for the *cis* and *trans* isomers of two mixtures of isomers incorporating the cyclobutane ring [structure (I), $X = \text{cyclobutane ring}$, $Y = \text{CN}$, $R = \text{C}_3\text{H}_7$ and C_5H_{11}]. The transition temperatures (and enthalpies) for these isomers are given in table 1. An interesting point to emerge from these results was that the order of S_A thermal stability was *cis* > *trans*, whereas the order of nematic thermal stability was *trans* > *cis*.

The cyclobutane group [2, 3] can exist in one of two puckered conformations with a typical dihedral angle of about 30°. It is able to invert between these conformations with an energy barrier that is typically about 6 kJ mol⁻¹. This is slightly greater than the mean thermal energy of a soft vibrational mode at room temperature (i.e. kT

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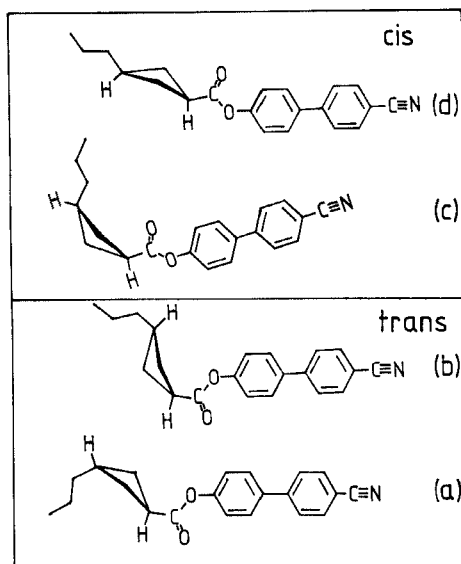


Figure 1. Possible conformations of the *trans* isomer of compound IIa (a) normal and (b) inverted and the *cis* isomer (c) normal and (d) inverted.

which is roughly 3 kJ mol^{-1} in the temperature range of interest here). Non-bonded and steric interactions are expected to influence which of the two puckered conformations is the more stable in a substituted cyclobutane molecule, and a liquid crystal environment may impose constraints on the situation. It is however possible that the energy barrier to inversion in a particular molecule might be lower than kT giving a flexible joint at the cyclobutane group. It is not possible to predict these factors reliably from inspection of the molecular formula, but we will refer to normal and inverted conformations for the two isomers and these are illustrated in figure 1. The aim of the work reported here was to discover if conformational changes of the cyclobutane group were responsible for the change in thermal stability order for the nematic phase as opposed to that for the smectic A phase. X-ray diffraction experiments on the nematic phase of the isomers illustrated in table 1 have been done in order to look for changes in the molecular length or molecular pairwise association of the cyano compounds as a function of temperature.

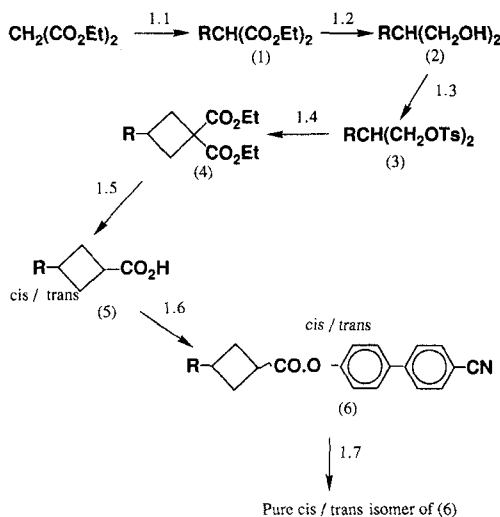
Table 1. Transition temperatures and enthalpies for compounds of structure (II).

Compound	Isomer	R	T_{CN} or $T_{\text{S}_{\text{A}}\text{N}}/^{\circ}\text{C}$ $\Delta H/\text{J g}^{-1}$		$T_{\text{Nl}}/^{\circ}\text{C}$ $\Delta H/\text{J g}^{-1}$
			T_{CN}	$T_{\text{S}_{\text{A}}\text{N}}$	
IIa	<i>cis</i>	C_3H_7	55.5	74.18	63.0, 0.92
	<i>trans</i>		47.5†	72.63	141.5, 1.46
IIb	<i>cis</i>	C_5H_{11}	40.0	64.94	63.5, 1.38
	<i>trans</i>		35.5	43.22	139.5, 1.63

† Preceded by a crystal-crystal transition at 40.5°C .

2. Preparation of materials

The reaction scheme used in the preparation of the cyclobutanes (II) is given here. Full experimental details of the synthesis and separation of the *cis* and *trans* isomers used in this investigation are given in [1].



- 1.1. *n*-RBr, NaOEt, EtOH
- 1.2. LiAlH₄, Et₂O
- 1.3. 4-Toluenesulphonyl chloride, C₅H₅N
- 1.4. CH₂(CO₂Et)₂, NaH, dioxan.
- 1.5. (i) KOH, EtOH, H₂O; (ii) H⁺; (iii) heat (decarboxylation).
- 1.6. (i) SOCl₂; (ii) HO-C₆H₄-C₆H₄-CN, Et₃N, CH₂Cl₂.
- 1.7. Partisil ODS II preparative HPLC column chromatography (80:20 mixture of methanol + water as eluant).

Reaction scheme.

3. Experimental results by X-ray diffraction

The X-ray scattering from aligned samples of the *cis* and *trans* isomers was recorded using graphite monochromatized copper *K*_α radiation and a two dimensional position sensitive detector [4]. The alignment was induced by cooling from the isotropic phase in a magnetic field of 1T. Figure 2 shows a schematic diffraction pattern in which there are two diffuse maxima in the direction parallel to the aligning field. Similar results have been observed with other nematics and have been interpreted as originating from two coexisting incommensurate density waves [5]. In order to analyse the data in terms of the wavelength and amplitude of these waves, we have taken a narrow horizontal strip across the centre of the diffraction pattern (where the scattering vector, *Q*, is essentially parallel to the field) and fitted the intensity distribution with the sum of two lorentzian functions (\mathcal{L}). A lorentzian shape for the peaks is expected if there are only short range correlations in the positions of the molecules along the director, *z*, so that the amplitude of the oscillation in the correlation function decays exponentially ($\sim \exp(-z/\xi)$) where ξ is the correlation length.

$$I(Q) = h_1 \mathcal{L}(w_1, q_1) + h_2 \mathcal{L}(w_2, q_2) + b, \quad (1)$$

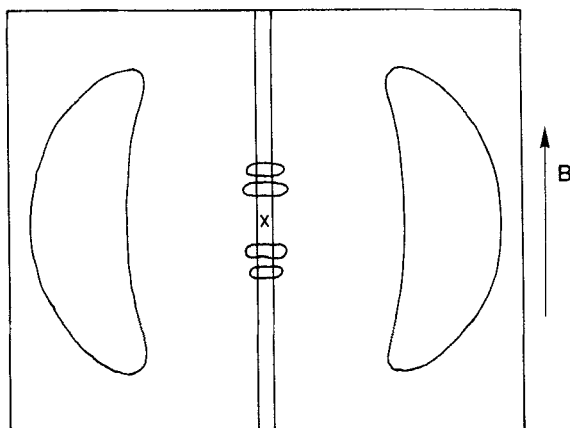


Figure 2. Outline X-ray diffraction pattern from the *cis* isomer of compound IIa (see table 1) at 25°C; an analogous pattern is given by the *trans* isomer. B shows the direction of the aligning magnetic field. The inner diffraction maxima are caused by end to end correlations of the molecules and have been analysed by taking a narrow strip across the diffraction pattern as shown.

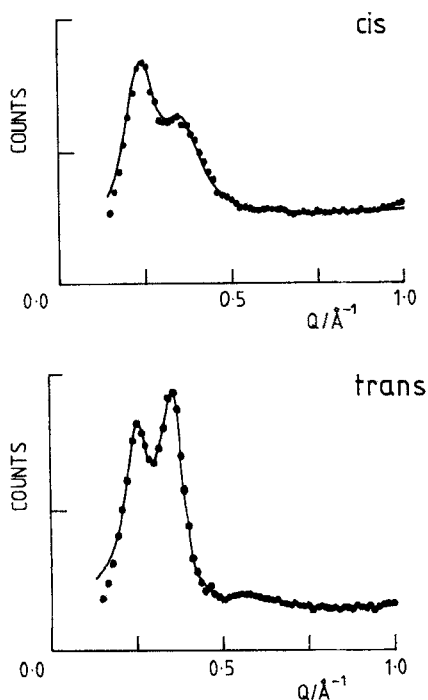


Figure 3. Fits of equation (1) to the intensities from a narrow horizontal strip across the diffraction pattern as shown in figure 2. The data from either side of the centre have been summed. The data are from (a) the *cis* isomer at 27°C and (b) the *trans* isomer at 40°C.

where

$$\mathcal{L}(w_i, q_i) = \frac{w_i^2}{w_i^2 + (Q - q_i)^2}$$

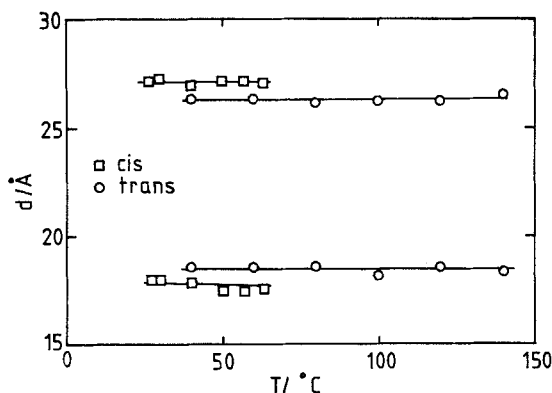


Figure 4. The wavelength ($d = 2\pi q^{-1}$) of the density wave from the *cis* (\square) and *trans* (\circ) isomers of compound IIa as function of temperature in the nematic phase.

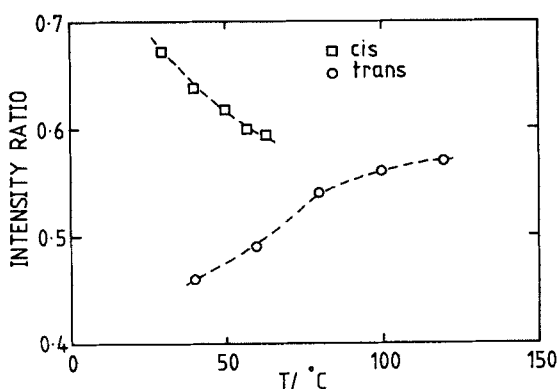


Figure 5. Ratio ($I_{\text{dimer}}/I_{\text{monomer}} + I_{\text{dimer}}$) of integrated intensities of the two meridional peaks in the X-ray scattering from the *cis* (\square) and *trans* (\circ) isomers of compound IIa as a function of temperature.

and w_i is the half width at half maximum of the i 'th lorentzian, h_i is its height and q_i is its position. A flat background, b , is also used.

Figures 3(a) and (b) show typical fits to the intensity distribution from the *cis* and *trans* isomers at a low temperature in the nematic phase. The positions of the two maxima appear to be independent of temperature as shown in figure 4. The widths of the two lorentzians were determined by the fit to the lowest temperature data and were found to be the same within experimental uncertainty. As the temperature increased, the widths also appeared to increase causing some merging of the peaks. For the high temperature data, the widths were kept at the ratio found at low temperature during the fitting procedure. These widths have been used to calculate correlation lengths

Table 2. Model molecular lengths (l), wavelengths of density waves and correlation lengths for isomers of compound IIa

Isomer	$l/\text{\AA}$	$2\pi q_1^{-1}/\text{\AA}$	$2\pi q_2^{-1}/\text{\AA}$	$\xi/\text{\AA}$
<i>cis</i>	21.1	27.2	18.0	16
<i>trans</i>	21.8	26.2	18.6	18

($\xi = w^{-1}$); the values (as shown in table 2) are typical for nematic phases. Their integrated intensities (i.e. the peak area, $I = hw\pi$) do have a marked temperature dependence which is different for the *cis* and *trans* isomers as shown in figure 5. It was not possible to make a clear separation into two peaks for the isotropic phase because the peaks had merged.

4. Discussion

The wavelengths of the two density waves are compared with an estimate of the extended molecular length (from CPK molecular models) in table 2. The density wave corresponding to q_2 is a few Angstroms shorter than the length of a molecule like the situation for a simple monomeric nematic. The density wave corresponding to q_1 can be interpreted as originating from overlapping core dimers as found for many nematics with terminal cyano groups [6]. We can therefore interpret the X-ray scattering in terms of a mixture of monomers and dimers. A more accurate description might be a mixture of regions with S_{A1} and S_{Ad} type short range order. The observation that these wavelengths are practically independent of temperature (see figure 4) indicates that there is no significant change in the conformation of the molecules in each state (i.e. monomeric and dimeric) over the nematic temperature ranges. The difference between the monomer wavelengths from the two isomers would indicate that the structure of the *cis* isomer is more bent giving a slightly shorter wavelength than that for the *trans* isomer. The difference between the dimer wavelengths indicates that in the *cis* isomer the molecules do not overlap so well, giving a longer dimer than the *trans* isomer.

We can interpret the changes in the intensities of the maxima as changes in the amounts of the monomer or dimer structure present. Figure 5 shows that in the *cis* isomer, the dimer is predominant at low temperatures in the nematic phase but the relative amount of it decreases as temperature increases. For the *trans* isomer there is less dimer than monomer, especially at low temperature, but the relative amount of it increases with rising temperatures. Since a dimer has an increased length to breadth ratio compared to a single molecule, it is generally understood that dimer formation enhances the stability of the nematic phase. It is most probably that this dimer formation is responsible for the higher clearing temperature of the *trans* isomer as compared to the *cis* isomer. The nematic phase of the *cis* isomer is lost at a lower temperature because of the dwindling number of dimers while for the *trans* isomer the nematic is stabilized at higher temperatures because of the increasing number of dimers.

The different thermal stabilities of the overlapping core dimers of the two different isomers is a striking result which we will attempt to explain. We could speculate that the *cis* dimers are not so stable because of their smaller overlap which perhaps leaves them vulnerable to being broken up by thermal agitation at higher temperatures. However it is not clear why the temperature dependence of the *trans* dimer population should be opposite to this. A more plausible explanation is that the relative populations of monomers and dimers is influenced by the conformation of the cyclobutane ring and we now propose a tentative model for this.

At low temperatures we suppose the ring to be puckered in its normal gaseous state as shown in figures 1 (*a*) and (*c*) and so (at least in a nematic environment) the *cis* molecule tends to be rather more bent than the *trans* molecule. This is borne out by the density wavelengths observed. We then assume that in a nematic environment,

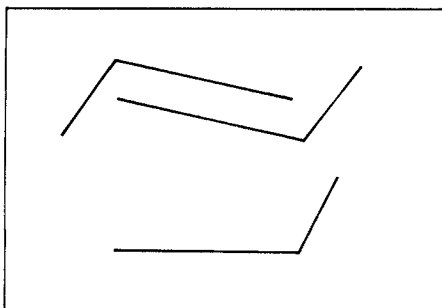


Figure 6. Schematic sketch of a bent monomer molecule and the overall straighter dimer.

the more bent molecules have a larger tendency to form dimers. This can perhaps be justified on grounds of more efficient filling of space with the straighter overall shape of the dimers than with bent molecules, as indicated in figure 6. At low temperature we would therefore expect more dimers in the *cis* isomer than the *trans* isomer, as observed. At higher temperatures, the ring spends more time in the inverted state since the difference between the normal and inverted states is comparable with mean thermal energy ($\sim kT$). This means that there will be a smaller population of bent *cis* molecules and the amount of dimer packing will decrease. However there will be a larger population of bent molecules in the *trans* isomer and so the population of dimers with an overall straighter shape will increase, as has also been observed in this work. The temperature independence of the density wavelengths confirms that all of the molecules are in one of only two conformations: i.e. with the normal puckered ring as shown in figure 1 (a) and (c) or with the cyclobutane ring inverted as shown in 1 (b) and (d). The population of intermediate conformations (which would have different lengths) is not significant which suggests that the energy barrier to inversion is at least $\sim 2kT$. This model also allows us to understand why the smectic A stability of the *cis* isomer is generally greater than the *trans* isomer. If the smectic is of type A_d (cf. the low enthalpy of the S_A-N transition) it will consist entirely of the overlapping cores type of packing which will be favoured by the *cis* isomer.

5. Conclusion

We have explained the enhanced nematic stability of the *trans* isomer in terms of an increase in the population of overlapping core dimers as the temperature increases. There is a loss in the thermal stability of the *cis*-isomer because of a decrease in the dimer population with increasing temperature. These population changes have been observed by X-ray scattering and can be rationalized theoretically by assuming two conformational types of each isomer (normal and inverted) and that the population of inverted molecules increases with temperature. We believe that this is the first time a temperature induced change in molecular conformation has been shown to influence directly the stability of the nematic phase.

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