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The Synthesis, Mesomorphic Behaviour and the Uniaxial Nature of 1,2,4,5-Tetra-(4-Alkoxybenzoyloxy) Benzenes

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THE SYNTHESIS, MESOMORPHIC BEHAVIOUR AND THE UNIAXIAL NATURE OF 1,2,4,5-TETRA-(4-ALKOXYBENZOYLOXY)BENZENES.

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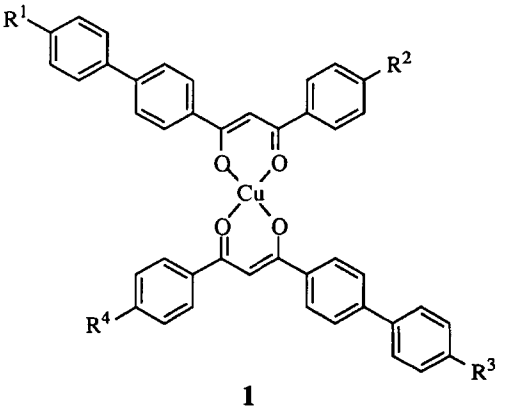
Abstract A homologous series of 1,2,4,5-tetra-(4-alkoxybenzoyloxy)benzenes (**2**, R = C_4H_9, C_6H_{13} to $C_{16}H_{33}$ and $C_{18}H_{37}$) has been synthesised. Optical microscopy revealed that the compounds with R = C_4H_9, C_6H_{13} to $C_{10}H_{21}$ have a nematic phase, compounds with R = $C_{11}H_{23}$ to $C_{14}H_{29}$ have nematic and smectic C phases and compounds with R = $C_{15}H_{31}$, $C_{16}H_{33}$ and $C_{18}H_{37}$ have only a smectic C phase. The T_{N-I} values show an 'odd-even' alternation which is typical of calamitic systems. The refractive indices for aligned samples of compound **2h** (R = $C_{10}H_{21}$) demonstrate that the nematic phase is uniaxial.

Introduction

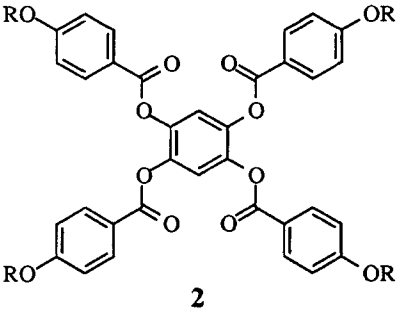
The discovery of thermotropic discotic liquid crystals[1,2] revealed a new major class of materials additional to the then-known lath-like, calamitic compounds. Since that time, numerous peculiarly shaped molecules have been reported and shown to have mesomorphic behaviour[3,4] which is characteristic of one or other of these two broad classes; the investigation of the properties of molecules which have structures on the boundary between calamitic and discotic liquid crystals is the subject of current interest and has been examined by a number of workers[5-10]. Several studies of copper(II) complexes of β-diketones (**1**) have revealed the interesting fact that some large cross-shaped molecules give calamitic nematic and smectic phases[11-14], whereas other coumpounds show discotic character[14].

(4-Alkoxybenzoyloxy)-substituted benzenes are another example of molecules which show discotic character for the hexa-substituted systems[1] and yet give monotropic calamitic nematic phases for compounds **2a-2c** (R = C_3H_7 to C_5H_{11})[5] (see Table 1).



1

As for compounds **1**, and some pyrones[15], the cross-shaped nature of the molecular structure seems conducive to liquid crystal formation and it was decided to further investigate compounds **2** with plans to ultimately vary the nature, number and flexibility of the substituents on the central benzene ring in order to test the possibility of preparing a biaxial nematic compound.



2

Transition Temperatures

A homologous series of compounds **2** with R = C_4H_9, C_6H_{13} to $C_{16}H_{33}$ and $C_{18}H_{37}$ was synthesised according to scheme 1 with the initial objective of obtaining enantiotropic mesophases or slightly monotropic mesophases for which their physical (principally optical) properties could be examined in a stable phase. Optical microscopy and DSC analysis of compounds **2b, d-o** (Table 1) confirmed that compounds **2b, d-h** have a nematic phase, compounds **2i-l** have nematic and smectic C phases and compounds **2m-o** have only a smectic C phase. A transition temperatures *vs* terminal chain length (C_n) plot (Figure 1) shows a clear 'odd-even' effect of T_{N-I} values and the gradual emergence of the smectic C phase from $C_{11}H_{23}$ onwards.

Table 1 also shows the variation in the enthalpies of transition with respect to increasing chain length. It is interesting to note that the clearing point enthalpy values rise with chain extension, as the transitions becomes more first-order. Similarly, the smectic C to nematic transition shows a strong rise in enthalpy value with increasing chain length. Both of these facets of phase transition behaviour suggest that as the peripheral chain lengths increase, there is an increasing disparity between the structure of the mesophase and that of the liquid. If the molecules remained in a disc-like conformation/structure throughout the series, then such a disparity might not be expected. T_{ND-I} transitions are usually weakly first-order because the local structure of the liquid is somewhat like that of the mesophase. Since the enthalpy values for compounds **2** rise strongly with chain length, showing an increasing structural difference between the mesophase and the liquid, it appears

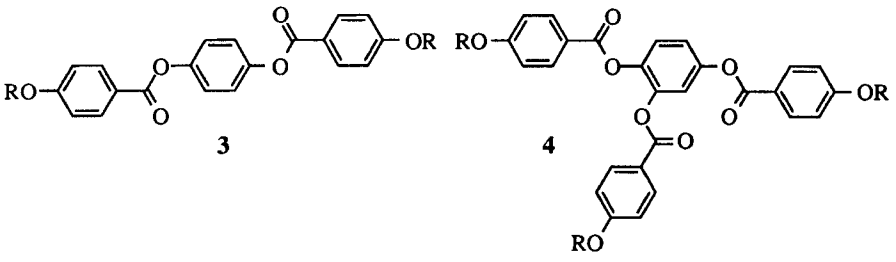
Compd No	OR	K		S_C		N		I
2a	OC_3H_7[a]	•	160 (45)	—	—	(•	115) (—)	•
2b	OC_4H_9[b]	•	123 (47.7)[c]	—	—	•	125 (0.99)	•
			123 *(72)*	—	—	(•	*121)* *(—)*	•
2c	OC_5H_{11}[a]	•	122 (59)	—	—	(•	103) (—)	•
2d	OC_6H_{13}	•	133 (56.64)	—	—	(•	107.8) (1.30)	•
2e	OC_7H_{15}	•	118 (55.14)	—	—	(•	104.5) (1.14)	•
2f	OC_8H_{17}	•	109.9 (61.68)	—	—	(•	105.4) (1.40)	•
2g	OC_9H_{19}	•	103.4 (59.0)	—	—	(•	100.9) (1.58)	•
2h	$OC_{10}H_{21}$	•	93 (58.61)	—	—	•	102 (1.77)	•
2i	$OC_{11}H_{23}$	•	100 (59.02)	(•	79.4 (4.48)	•	99.6) (2.15)	•
2j	$OC_{12}H_{25}$	•	102.5 (61.23)	(•	88.5 (5.87)	•	100.2) (2.19)	•
2k	$OC_{13}H_{27}$	•	97.8 (58.29)	(•	94.3) (6.33)	•	100 (2.32)	•
2l	$OC_{14}H_{29}$	•	97.2 (65.26)	•	98.9 (8.18)	•	100 (2.68)	•
2m	$OC_{15}H_{31}$	•	95.1 (66.46)	•	100 (12.35)	—	—	•
2n	$OC_{16}H_{33}$	•	96.5 (74.6)	•	101.5 (14.31)	—	—	•
2o	$OC_{18}H_{37}$	•	98.5 (84.9)	•	101.6 (15.80)	—	—	•

a...values are from reference 5; b...reported values for **2b** in reference 5 are given in italics; c...transtion enthalpies in kJ mol^{-1}

Table 1. Transition Temperatures (°C) and Enthalpies of Transition (kJ mol^{-1}) for compounds 2a - 2o.

that the molecules are developing a more distinct anisotropic shape. This could be due to the peripheral arms on the same side of the molecule lying parallel to one another to give a rod-like structuring; increasing the chain length under these circumstances will lead to increasing molecular anisotropy and thereby possibly to an increase in enthalpy. Thus at shorter chain length we might expect the molecules to have more of a disc-like shape, but upon chain extension they become rod-like.

Some examples of the 1,4,-di(4-alkoxybenzyloxy)benzenes (**3**)[16,17] and the 1,2,4-tri(4-alkoxybenzoyloxy)benzenes (**4**)[8] have already been reported and the values for transition temperatures also reinforce the view that a cross-shaped structure gives a suprising enhancement of mesogenicity. For example, the transtion temperatures for



3 4

the $C_8H_{17}O$-$C_{10}H_{21}O$ substituted compounds (see Table 2) show that lateral substitution in compound **3** to give the 1,2,4-system (compound **4**) leads to complete eradication of mesogenicity (a depression of at least 144.0, 139.0, and 132.6 °C respectively). On the other hand, when the second lateral group is introduced to give the cross-shaped compounds **2**, the mesogenicity relative to compound **4** is increased by at least 54.5, 53.5 and 52.9 °C respectively. Even comparison of the values for compounds **2** and **3** shows that the reduction in T_{N-I} values is much less than expected for normal lateral substitution[18,19].

OR	Compd No	K		S_C		N		I
	3	•	121.9	•	125.6	•	194.9	•
OC_8H_{17}	4	•	50.9	—	—	—	—	•
	2f	•	109.9	—	—	(•	105.4)	•
	3	•	128.4	•	135.7	•	186.4	•
OC_9H_{19}	4	•	47.4	—	—	—	—	•
	2g	•	103.4	—	—	(•	100.9)	•
	3	•	126.7	•	146.6	•	181.7	•
$OC_{10}H_{21}$	4	•	49.1	—	—	—	—	•
	2h	•	93	—	—	•	102	•

Table 2. Transition Temperatures (°C) for some examples of Compounds 2, 3 and 4.

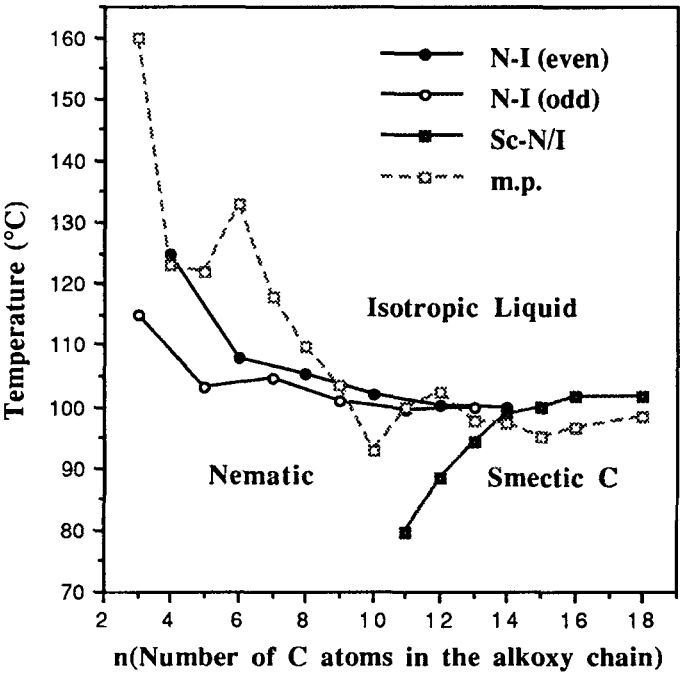
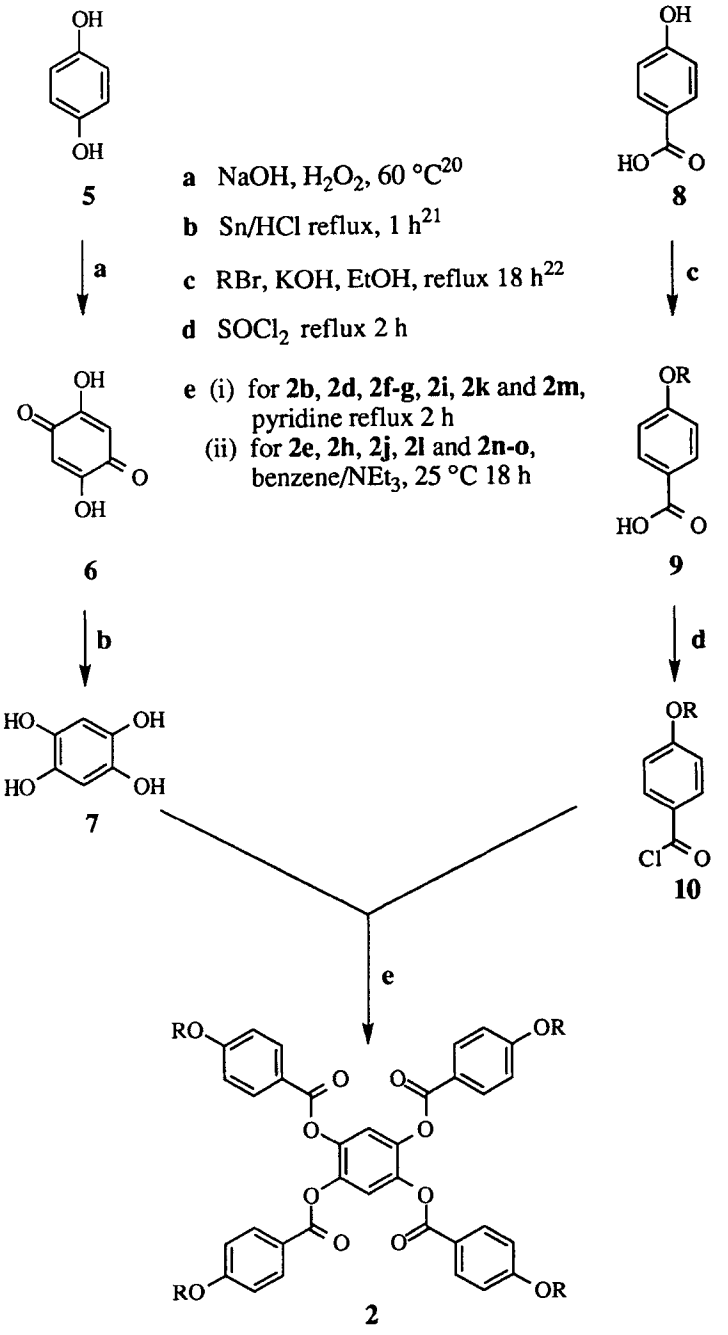


Figure 1. Phase Transition Temperatures vs n for compounds 2a-o.

Alignment

For the study of the optical properties of the nematic phase of these compounds, compound **2h** (the $C_{10}H_{21}$ homologue) was chosen which has a wide nematic phase on cooling (I 102 N 86 K). Homeotropic alignment was attempted using a 1.9 μm spaced cell with a chrome-complex ($C_{16}H_{33}CO_2Cr_2Cl_4OH$) mono-layer spun onto the ITO surface. The texture observed in the nematic phase by polarised light microscopy was the characteristic *schlieren* texture, due to a component of birefringence in the plane of the cell. This birefringence either represents the difference of the two transverse refractive indices of a biaxial nematic phase, if the nematic director, **n**, is substantially aligned by the homeotropic surfactant, or it is due to misalignment of the **n** director in a uniaxial nematic phase.

The texture was also studied in thin, rubbed, polymer-aligned samples, using both a polyimide (PROBIMIDE 32, ® CIBA-GEIGY) and poly(vinyl alchohol) (PVA). Excellent planar, homogeneous alignment was obtained, with either polymer leading to a uniform monodomain across the cell. These results confirm the calamitic nature of the compound, since these polymer alignment layers give homeotropic alignment of discotic nematic materials[23]. Despite having a texture typical of uniaxial nematic materials, with a uniform birefringence colour across the area of the cell, this does not necessarily require the nematic phase to be uniaxial; a uniform texture would result if the polymer surfactant also aligns the tranverse axes of a biaxial material. This issue was tested using critical angle measurements as described in the following section.



Scheme 1

Refractive Indices

The refractive index tensor of the biaxial nematic has three principal components, n_1, n_2 and n_3. Assuming the biaxial nematic has orthorhombic symmetry, then n_3 is along the director representing the orientational order of the long molecular axis, and n_1 and n_2 are along the directors representing orientational order of the two transverse axes. Refractive index measurements were made using an Abbé refractometer (Bellingham and Stanley, 60 HR). Aligned samples were prepared by coating the prisms with PVA and rubbing with a tissue. The rubbing direction **r** was arranged either parallel or perpendicular to the direction of incident light **i**. In the **r**⊥**i** geometry, the measured extraordinary index is n_3, and the ordinary index corresponds to either n_1 or n_2 depending on which component is aligned perpendicular to the surface by the alignment layer. This is shown in figure 2 where it is assumed that the PVA aligns the material with n_1 perpendicular to the surface layer. None of the following conclusions are changed if the indices n_1 and n_2 are interchanged. The ordinary and extraordinary indices measured in the **r**||**i** geometry correspond directly to n_1 and n_2, and this geometry provides a direct observation of whether the phase is optically biaxial or not.

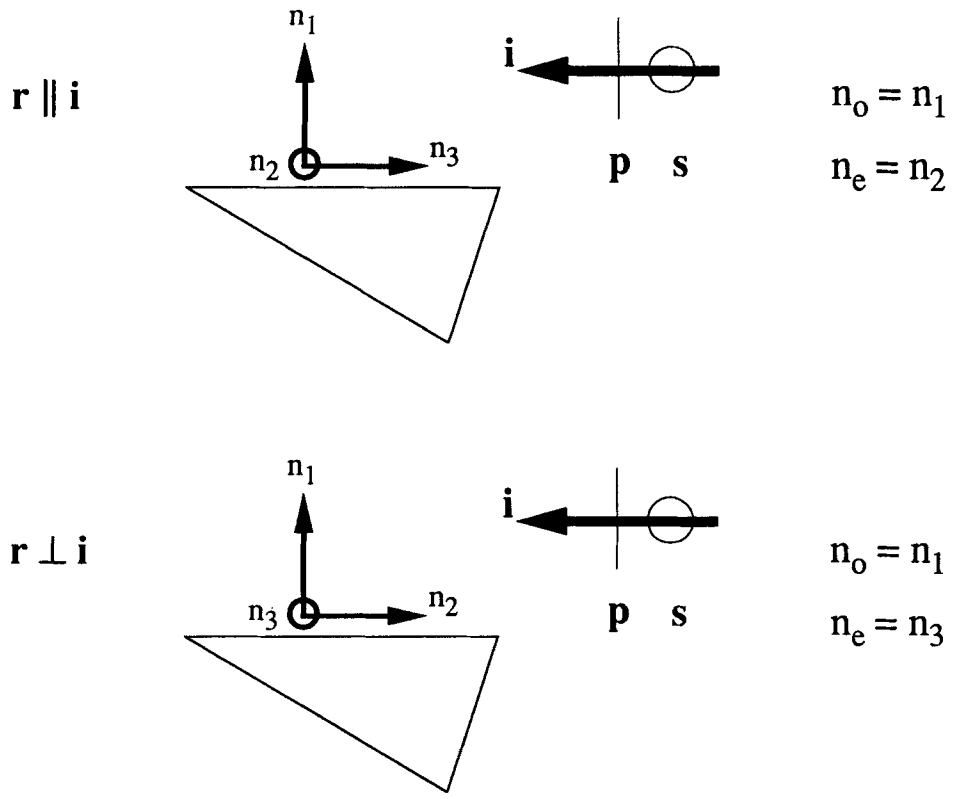


Figure 2. Refractive index measurements for an aligned biaxial nematic.

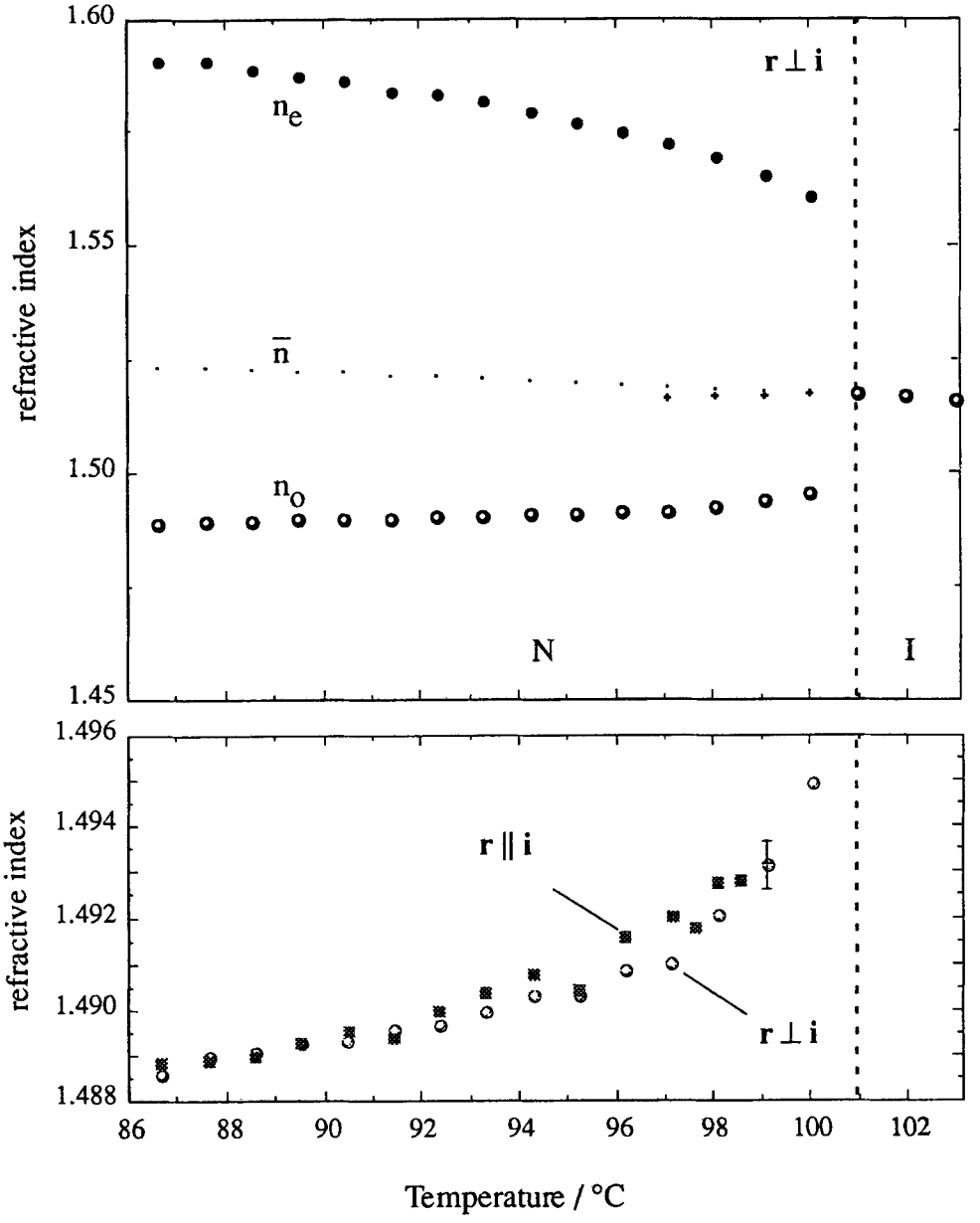


Figure 3. Temperature Dependence of the Refractive Indices for Compound 2h at 589.6nm.

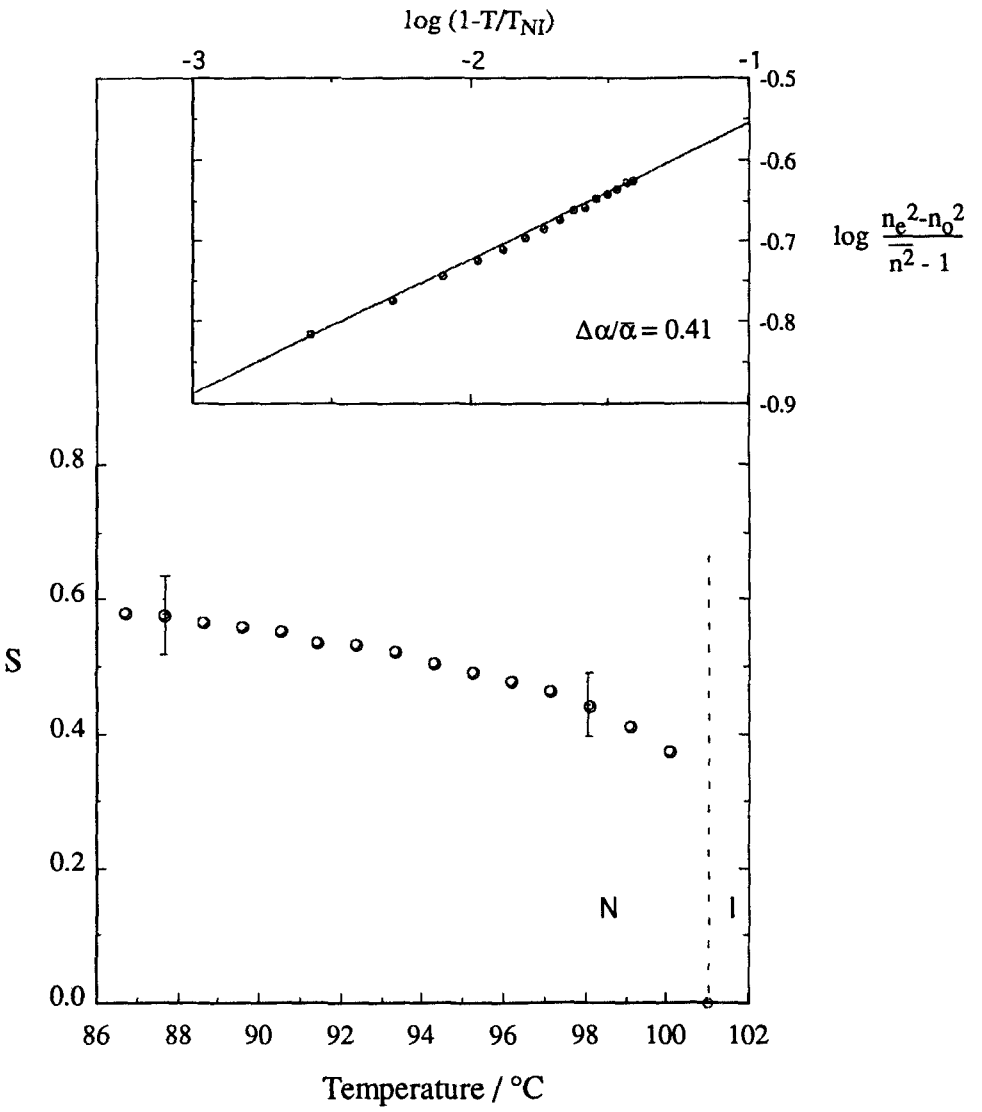


Figure 4. Temperature dependence of the Order Parameter calculated from the Refractive Index data using the Haller plot (inset).

The results for compound **2h** (the $C_{10}H_{21}$ homologue) are shown in figure 3. In the **r**||**i** geometry, on cooling through the isotropic liquid to the transition to the nematic phase, a single demarcation line was observed which was independent of the polarisation of the incident light. This clearly indicates that the nematic phase is uniaxial (*i.e.*, $n_1 = n_2 = n_o$). Thus, the refractive indices measured in the **r**⊥**i** geometry are the uniaxial indices n_o and n_e. Moreover, shearing the sample by lightly tapping the prisms[24] did not disturb the ordinary refractive index line, again indicating a uniaxial nature of the nematic phase. (One area of the refractometer field of view gave a line corresponding to the isotropic refractive index below the clearing point, due to the large biphasic nature of the transition). The birefringence Δn

($= n_e - n_o$) is positive, supporting the conclusion that the nematic phase is calamitic. The spherical mean refractive index $\bar{n}$ ($= {}^1/_3\, n_e + {}^2/_3\, n_o$) is also shown in figure 3.

The refractive index data was used to calculate the S order parameter using the Vuks approximation[25], with a Haller extrapolation to calculate the molecular polarisability relationship $\Delta\alpha/\bar{\alpha}$[26]. The large uncertainty associated with determining $\Delta\alpha/\bar{\alpha}$, and therefore S, is associated with the uncertainty of determining the clearing point for a material with a wide biphasic region. However, the results do indicate that the order parameter is typical of nematic materials. The material's birefringence is small and, as for recent measurements made on a discotic nematic[27], this is not due to a lower S order parameter, but may be due to intermolecular rotations of the substituted benzene rings. Alternatively, if the molecule is rigid and orthorhomboidal, the refractive indices may be affected by the increased molecular order parameter D[28,29].

Conclusion

The nematic phase of compound **2h** has been shown to be uniaxial using simple, critical angle refractometry. This result augments recent NMR evidence[30], using a spinning magnetic field to orient the system, which suggested that similar materials are uniaxial or extremely weakly biaxial. Previous reports of optical biaxiality probably arise from the difficulty in obtaining homeotropic alignment, and a misalignment of the uniaxial optical axis away from the surface normal.

There is a continuing difficulty in synthesising a thermotropic biaxial nematic phase. Further modifications may be envisaged in which the molecules are extended along the transverse axis, with the molecule made more rigid, but obtaining the biaxial nematic phase is likely to require very close control of the molecular dimensions.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H and ^{13}C NMR spectroscopy (JEOL JNM-GX270 spectrometer), and infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer). The progress of reactions was frequently monitored by thin layer chromatography using aluminium-backed silica gel plates (60 F254 Merck). Column chromatography was performed using Fisons 60-120 mesh silica gel and flash chromatography using May and Baker Sorbsil® C60 40-60 H micron silica gel. Transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station). The purities of each final compound were checked by HPLC analysis (Microsorb C18 80-215-C5 RP column) and were found to be >99% pure in each case.

The preparations of intermediates **6**[20], **7**[21] and **9**[22] have been previously reported and compounds **10** were prepared in a standard manner from the acids.

Compounds **2b, d-o** were synthesised according to two general methods; examples of the syntheses are given below and all the final esters showed similar spectral properties to those for compounds **2d** and **2l**.

1,2,4,5-Tetra-(4-hexyloxybenzoyloxy)benzene (2d)
4-Hexyloxybenzoyl chloride (**8d**) (928 mg, 0.45 mmol) and 1,2,4,5-tetrahydroxybenzene (**5**) (145 mg, 1.0 mmol) were suspended in dry pyridine (10 ml) and the mixture was heated under reflux for 2 h. The reaction mixture was then poured in to 1N-HCl (10 ml) cooled in ice, washed with dichloromethane (2x 15ml) and the combined organic layers were washed with water (2x 20ml), with saturated

aqueous sodium hydrogencarbonate (2x 15 ml) and with aqueous sodium chloride (15 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a thick oil which was treated with light petroleum (bp 40-60 °C) (5ml) and the white precipitate formed was collected, dried, and chromatographed on silica (dichloromethane) and recrystallised (acetone) to give colourless needles (730 mg, 75%); K 133 (N 107.8) I (°C); δ ($CDCl_3$) 8.01(d, 8H, ArH, J = 9.04 Hz), 7.49(s, 2H, Ar), 6.84(d, 8H, ArH, J = 9.04 Hz), 3.98(t, 8H, OCH_2, J = 6.4 Hz), 1.80(m, 8H, CH_2), 1.3(m, 48H, CH_2), 0.90(t, 12H, CH_3, J = 6.8 Hz). IR (KBr, cm^{-1}) 2917, 2849, 1726, 1601, 1573, 1508, 1489, 1467.

1,2,4,5-Tetra-(4-tetradecyloxybenzoyloxy)benzene (2l)

4-Tetradecyloxybenzoyl chloride (2.73 g, 7.73 mmol) and 1,2,4,5-terahydroxybenzene (5) (250 mg, 1.76 mmol) were suspended in dry benzene (10 ml); dry triethylamine (1.08 ml) was added and the mixture was stirred at room temperature for 18 h. The reaction mixture was then poured into water (20 ml) and the mixture was washed with dichloromethane (2x 20 ml); the combined organic layers were washed successively with 1N-HCl (2x 10 ml), water (2x 20 ml), aqueous sodium hydrogencarbonate (2x 20 ml) and saturated aqueous sodium chloride (2x 20 ml). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give an off-white solid which was treated with light petroleum (bp 40-60 C) (10 ml) and filtered to give a product which was chromatographed over silica (dichloromethane) and recrystallised (acetone) to give colourless needles (1.5 g, 60%); δ ($CDCl_3$) 8.01(d, 8H, ArH, J = 8.69 Hz), 7.49(s, 2H, Ar), 6.84(d, 8H, ArH, J = 8.69 Hz), 3.98(t, 8H, OCH_2, J = 6.6 Hz), 1.80(m, 8H, CH_2), 1.3(m, 48H, CH_2), 0.88 (t, 12H, CH_3, J = 6.8 Hz).δ (^{13}C, $CDCl_3$) 163.6 (C=O), 140.14 (ArC), 132.41 (ArC), 120.67 (ArC), 118.47 (ArC), 114.26 (ArC), 68.31 (OCH_2), 31.96 (CH_2), 29.7-29.1(m, CH_2), 26.0 (CH_2), 22.72 (CH_2), 14.15 (CH_3). IR (KBr, cm^{-1}) 2917, 2849, 1726, 1601, 1573, 1508, 1489, 1467.

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