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

The synthesis and characterization of novel non-symmetric dimers with rod-like and disc-like mesogenic units

I. D. Fletcher[ab]; G. R. Luckhurst[a]
[a] Department of Chemistry, University of Southampton, Southampton, England [b] Departimento de Quimica Orgánica, Facultad de Ciencias, Universidad de Zaragoza, Zara-goza, Spain

To cite this Article Fletcher, I. D. and Luckhurst, G. R.(1995) 'The synthesis and characterization of novel non-symmetric dimers with rod-like and disc-like mesogenic units', Liquid Crystals, 18: 2, 175 — 183

To link to this Article: DOI: 10.1080/02678299508036611

URL: http://dx.doi.org/10.1080/02678299508036611

LIQUID CRYSTALS, 1995, VOL. 18, NO. 2, 175–183

The synthesis and characterization of novel non-symmetric dimers with rod-like and disc-like mesogenic units

by I. D. FLETCHER† and G. R. LUCKHURST*
Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England

(*Received 9 June 1994; accepted 27 June 1994*)

Theory predicts that a compound whose structure possesses both rod-like and disc-like characteristics should exhibit a biaxial nematic phase. With this in mind we have synthesized and characterized two new series of non-symmetric dimers containing rod-like and disc-like mesogenic units linked by a flexible spacer. The two series differ in that in one the perimeter of the disc-like unit is decorated with alkyl chains, whereas for the other it is not. The liquid crystalline properties of the two series were investigated both as pure systems and in their equimolar binary mixtures with an electron acceptor. The nematic phase formed by the equimolar binary mixtures is monotropic. However, a small entropy change at the nematic-isotropic transition could be determined. The nature and structure of the monotropic nematic phase is discussed.

1. Introduction

Despite the theoretical prediction in 1970 of the existence of the biaxial nematic phase for thermotropic mesogens, experimental support for this prediction has been limited [1]. The first report was not until 1986 when Malthête *et al.* [2], claimed that 4-[3′,4′,5′-tri(*p*-*n*-dodeclyoxybenzyloxy)]-benzoyloxy-4″-*p*-*n*-dodeclyoxybiphenyl exhibited both uniaxial and biaxial nematic phases (both phases were monotropic). The assignment of the biaxial nematic phase was made on the basis of its optical texture which showed characteristic zigzag discli-nation lines and from its X-ray diffraction pattern. However, in contrast to theoretical predictions [1], the phase sequence on cooling was isotropic–biaxial nematic–uniaxial nematic and not isotropic–uniaxial nematic–biaxial nematic. In addition the biaxial nematic-isotropic transition was found to be weak, but first order, whereas theory predicts it to be second order. Subsequently the low temperature nematic has been identified as a smectic C phase [3] and by implication it seems likely that the high temperature phase is a uniaxial nematic. Later Chandrasekhar *et al.* [4], claimed the existence of a monotropic biaxial nematic phase for a copper complex; again the biaxial nematic phase underwent a transition directly into the isotropic phase and was identified by conoscopy. Much work on the synthesis of compounds with a large molecular shape biaxiality has been conducted by Praefcke and his group. They have synthesized the compounds [(1, 2, 3, 5, 6-pentakis(4-pentylphenylethynyl))benzene-4′-oxy]nonane and α-ω-bis[(1,2,3,5,6-pentakis(4-pentylphenylethynyl))benzene-4′-oxy]dodecane and, based on conoscopic studies, reported them to exhibit a biaxial nematic phase [5]. In both cases there was a direct isotropic-biaxial nematic phase transition, which from DSC studies was found to be weakly first order. Later Praefcke and his colleagues reported 2,3,4-trihexyloxycinnamic acid to exhibit a biaxial nematic phase [5, 6]. Again the phase assignment was made on the basis of conoscopic observations and an unusual X-ray diffraction pattern.

The biaxial nematic phases claimed in the literature thus far have been principally characterized on the basis of conoscopic studies. However, in every case, the cross, produced in the extinction position, was observed to split into two hyperbolic brushes whose centres remained in close proximity after a 45° rotation of the microscope stage, thus indicating a small optical biaxiality. This is in stark contrast to the conoscopic observations of the biaxial nematic phase produced by the lyotropic liquid crystal reported by Yu and Saupe [7] where the centres of the brushes were seen to approach the edges of the microscopic field of view, which demonstrates a large optical biaxiality. Indeed such differences have been further supported by deuterium NMR experiments in which the phase biaxiality was shown to be very large for the lyotropic liquid crystal reported in [7] and, within experimental error, zero for 2,3,4-trihexyloxycinnamic acid [8]. So far, therefore, no thermotropic liquid crystal has been reported to exhibit a nematic phase with significant optical or quadrupolar biaxiality.

---

*Author for correspondence.

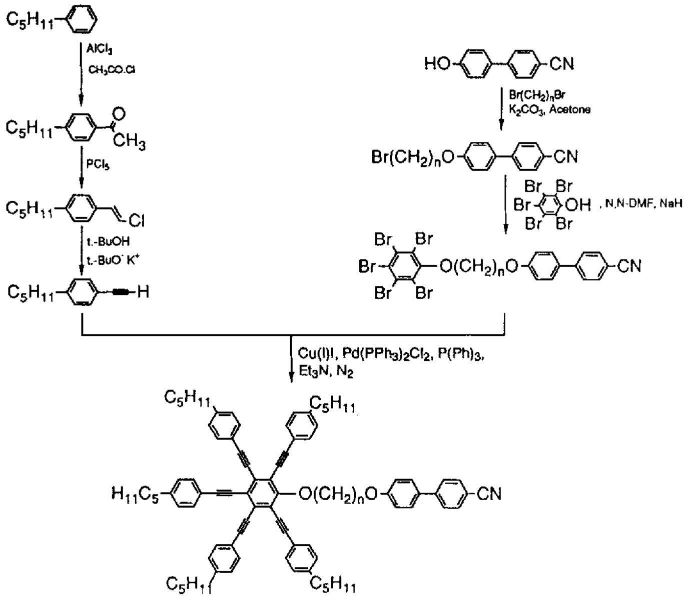
†Present address: Departimento de Quimica Orgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain.

Theoreticians have suggested an alternative route to forming the elusive thermotropic biaxial nematic phase and that is to mix rod-like with disc-like molecules [9]. However, in practice this prediction has proven to be unsuccessful as separation into two uniaxial nematics occurs, one rich in rod-like and the other in disc-like molecules [10]. In contrast, computer simulations of model mixtures have confirmed the existence of the biaxial nematic phase for such mixtures, since now the ability of the mixture to phase separate has been removed [11]. The experimental problem of phase separation can be circumvented by linking both the disc-like and rod-like molecules together via a flexible spacer. To date no attempt has been made to test this hypothesis for rod-disc dimers although the molecules of the compound made by Malthête *et al.* [2], do resemble the fusion of a semi-circle with a rod to give a rigid unit. In consequence, we have chosen to synthesize the first rod-disc dimers by joining together the disc-shaped [pentakis(4-pentylphenylethynyl)]benzene and the rod-shaped 4-cyanobiphenyl moieties through an ether-linked, flexible alkyl spacer: here we present our results for the α-[(1,2,3,5,6-pentakis(4-pentylphenylethynl))-benzene-4-oxy]-ω-(4′-cyanobiphenyl-4-yloxy)alkanes. This electron-donating disc was chosen as compounds with this moiety have also shown interesting phase behaviour when doped with an electron-accepting compound [12]. Thus by studying this system, the possibility of phase induction with the electron acceptor 2,4,7-trinitro-9-fluorenone (TNF) exists if the system itself is not naturally mesogenic. We have also extended our knowledge of such electron donor-acceptor complexes by comparing this system with mixtures of the similarly structured α-[(1,2,3,5,6-pentakis(4-phenylethynyl))benzene-4-oxy]-ω-(4′-cyanobiphenyl-4-yloxy)alkanes with TNF. These compounds, which are not expected to be mesomorphic in the pure state, because of their anticipated high melting points, allow a comparison of the influence of the perimeter alkyl chains on the phase behaviour of the binary mixtures.

For convenience the α-[(1,2,3,5,6-pentakis(4-pentylphenylethynyl))benzene-4′-oxy]-ω-(4′-cyanobiphenyl-4-yloxy)alkanes and the α-[(1,2,3,5,6-pentakis(4-phenylethynyl))benzene-4′-oxy]-ω-(4′-cyanobiphenyl-4-yloxy) alkanes are denoted by 5DO*n*OCB and DO*n*OCB, respectively, where 5 indicates a pentyl chain, D is a disc, CB is cyanobiphenyl and *n* is the number of methylene groups in the alkyl spacer.

2. Experimental

The reaction scheme outlines the synthetic pathway to the 5DO*n*OCBs and we describe in detail the preparation of 5DO6OCB as an example. The synthesis of the DO*n*OCBs proceeds in a similar manner. The syntheses of 4-pentylacetophenone, 1-(4-pentylphenyl)-2-chloroethene and the α-bromo-ω-(4′-cyanobiphenyl-4-yloxy)-alkanes can be found in [13], [14] and [15], respectively. All intermediates were structurally characterized by IR (Perkin-Elmer 1600 series FTIR spectrometer) and ^{1}H NMR spectroscopy (JEOL FX90Q Fourier transform NMR spectrometer). In addition, the final products were characterized by ^{1}H NMR with a Bruker AM 360 MHz NMR spectrometer, mass spectroscopy (VG 70-250) and elemental analysis. The liquid crystal optical textures were investigated using an Olympus BH-2 optical microscope fitted with a TMS90 Linkham hot stage and the thermal behaviour of the phase transitions was examined with a Perkin-Elmer DSC7 differential scanning calorimeter.



The synthetic route to the 5DO*n*OCB series (the route to the DO*n*OCB series is essentially the same).

2.1. *Synthesis of 4-pentylphenylacetylene [16]*

1-(4-Pentylphenyl)-2-chloroethene (30·2 g, 0·15 mol) and potassium *tert*-butoxide (59·5 g, 0·53 mol) were heated under reflux in *tert*-butanol (650 ml) for 36 h at 110°C in an oil bath. After cooling, the reaction mixture was poured on an ice/water mixture and shaken with diethyl ether (4 × 100 ml). The combined ether extracts were washed with aqueous sodium chloride solution (4 × 100 ml) and dried over anhydrous magnesium sulphate. After filtration and evaporation of the solvent, the crude product was distilled under vacuum using a Kugelrohr apparatus. The colourless fraction boiling at 110°C (1 mb) was collected. Yield 14·8 g (57 per cent).

IR (NaCl disc, neat): ν/cm^{-1} 2109 (C≡C), 3296 (H–C≡). ^{1}H NMR ($CDCl_3$): δ/ppm 0·8–1·0 (t, 3 H) 1·1–1·8 (m, 6 H), 2·5–2·7 (t, 2 H), 3·0 (s, 1 H), 7·0–7·2 (d, 2 H), 7·3–7·5 (d, 2 H).

2.2. *Synthesis of α-(1,2,3,5,6-pentabromobenzene-4-oxy)-ω-(4-cyanobiphenyl-4′-yloxy)hexane*

Sodium hydride (0·29 g, 9·6 mmol) and pentabromophenol (3·8 g, 8·0 mmol) were warmed in 50 ml of dry *N*,*N*-dimethylformamide (4 Å molecular sieves) and then stirred for one hour in a reflex apparatus. α-Bromo-ω-(4′-cyanobiphenyl-4-yloxy)hexane (4 g, 11·2 mmol) was then added and the reaction mixture heated to 80°C and stirred for 26 h. After cooling, the mixture was poured into water and the resulting precipitate was filtered off and dried *in vacuo*. The crude solid was recrystallized twice from acetone to give white crystals. Yield 5·5 g (65 per cent), $T_{CI} = 150$°C, $T_{NI} = 52$°C (monotropic). The transition temperatures of the remaining homologues are given in table 1. IR NaCl disc, film): ν/cm^{-1} 2224 (–C≡N). ^{1}H NMR ($CDCl_3$): δ/ppm 1·4–2·0 (m, 8 H), 3·8–4·1 (m, 4 H), 6·9–7·0 (d, 2 H), 7·4–7·5 (d, 2 H), 7·6 (s, 4 H).

2.3. *Synthesis of α-[(1,2,3,5,6-pentakis (4-pentylphenylethynyl))benzene-4-oxy]-ω-(4′-cyanobiphenyl-4-yloxy)hexane*

α-(1,2,3,5,6-Pentabromobenzene-4-oxy)-ω-(4′-cyanobiphenyl-4-yloxy)hexane (1·54 g, 2·0 mmol), 4-pentylphenylacetylene (3·5 g, 20 mmol), copper (I) iodide (70 mg, 0·4 mmol), triphenylphosphine (120 mg, 0·5 mmol) and bis(triphenylphosphine)palladium (II) chloride (70 mg, 0·1 mmol) were heated under reflux in degassed triethylamine (30 ml) in an oil bath at 110°C under nitrogen for 15 h. The nitrogen gas was introduced via an inlet needle and exited through a bubbler. After cooling, the reaction mixture was poured into 5 M hydrochloric acid (200 ml). Organic material was extracted with dichloromethane (4 × 50 ml) and the combined extracts were dried over anhydrous sodium sulphate. Evaporation of the solvent gave a dark brown oil which solidified when washed with petroleum ether. The resultant light brown solid was filtered off and purified by flash chromatography (silica gel 60) using chloroform/petroleum ether (3 : 2) as eluent. Two recrystallizations from acetone gave pale yellow crystals. A solution of the crystals in chloroform showed blue fluorescence. Yield 0·9 g (36 per cent). IR (NaCl disc, film): ν/cm^{-1} 2202 (–C≡C–), 2227 (–C≡N). ^{1}H NMR ($CDCl_3$): δ/ppm 0·8–1·1 (t, 15 H), 1·2–2·1 (m, 38 H), 2·5–2·8 (m, 10 H), 3·8–4·0 (t, 2 H), 4·4–4·5 (t, 2 H), 6·8–7·0 (d, 2 H), 7·1–7·3 (m, 10 H), 7·4–7·7 (m, 16 H). MS (Argon FAB): 154 (100 per cent), 1222 (M^+, 5 per cent). Elemental analysis: calculated C 88·45, H 7·78, N 1·15; found C 88·08, H 7·81, N 1·16 per cent.

Table 1. The transition temperatures for the α-(1,2,3,5,6-pentabromobenzene-4-oxy)-ω-(4-cyanobiphenyl-4′-yloxy) alkanes.

	T/°C	
n	C–I	N–I
6	150	(52)
7	114	
8	122	(52)
9	88	
10	125	
11	102	(33)
12	100	(54)

Parentheses indicate a monotropic transition.

2.4. *Analysis of the phase behaviour of the dimers by contact preparations with TNF*

Contact preparations were made by first melting the compound with the highest melting point on a glass slide and covering with a cover slip. Then the lower melting compound was placed on the side of the cover slip and melted. Through capillary forces the compound flowed under the cover slip and made contact with the other component. This was clearly seen by the formation of an orange-red band, resulting from a charge-transfer interaction between the acceptor and donor species. Across this band there was a concentration gradient making it possible to observe the phase behaviour of different binary compositions with temperature.

2.5. *Preparation of equimolar mixtures of the dimers with TNF*

Equimolar mixtures were prepared by weighing the calculated, mol percentage amounts of the dimers derivatives and dry TNF (dried by dissolving in dichloromethane over anhydrous sodium sulphate). The two components were mixed by dissloving them in dry dichloromethane, when a yellow to deep orange–red colour developed. The dichloromethane was first allowed to evaporate by leaving the solution to stand overnight and then final traces were removed by placing the sample overnight in a vacuum oven (25°C, 1 mb); an orange-red solid was produced.

3. Results and discussion

3.1. *The 5DOnOCB series*

Table 2 summarizes the transitional behaviour of seven members of the 5DO*n*OCB series. From the table we see that, except for one compound, there is no liquid crystalline behaviour exhibited by this series. The $n = 6$

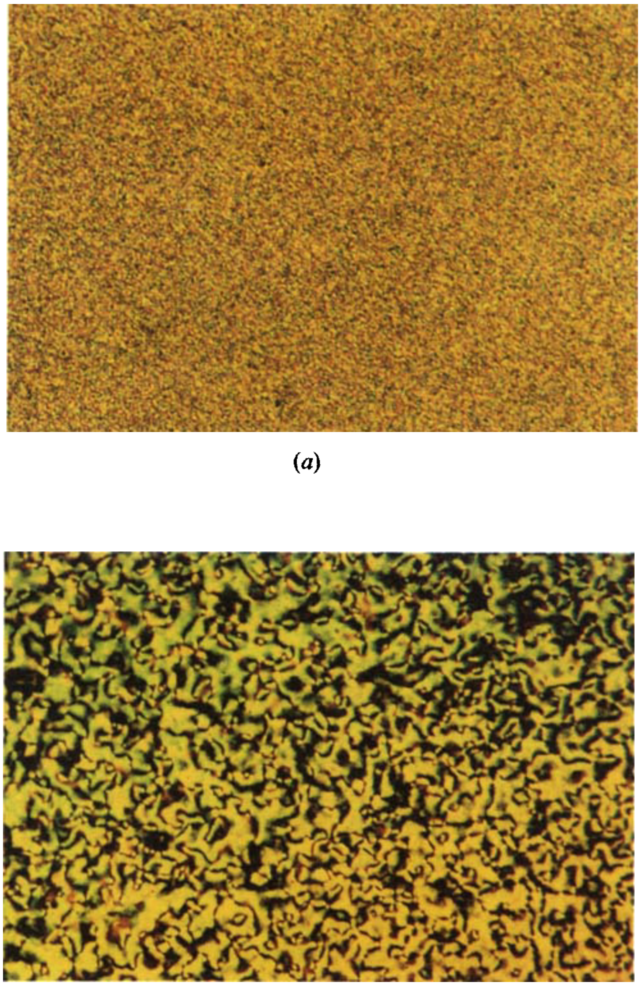
Table 2. The transition temperatures, enthalpies and entropies of the 5DO*n*OCB series and their equimolar mixtures with TNF.

	5DO*n*OCB			5DO*n*OCB + TNF (50 : 50 mol%)					
n	T_{CI}/°C	ΔH_{CI}/kJ mol^{-1}	ΔS_{CI}/R	T_{CI}/°C	T_{NI}/°C	ΔH_{CI}/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}	ΔS_{CI}/R	ΔS_{NI}/R
6	125†	48·5	14·56	62	(48)	19·5	(0·3)	6·99	(0·13)
7	111	52·8	16·59	77	(42)	19·9	(0·3)	6·83	(0·10)
8	98	56·5	18·28	76	(37)	26·9	(0·3)	9·27	(0·10)
9	85	43·2	14·51	76	(12)	24·4	(0·3)	8·40	(0·14)
10	65	47·0	16·73	46	(29)	22·8	(0·3)	8·59	(0·11)
11	76	51·2	17·67	41	(18)	19·6	(0·6)	7·51	(0·23)
12	63	45·1	16·06	41	(24)	20·9	(1·0)	8·00	(0·42)

† From polarizing microscopy a nematic phase was observed at 79°C by supercooling isolated droplets.
Parentheses indicate a monotropic transition.

homologue exhibits a monotropic nematic phase at 79°C, which is approximately 45°C below the melting point; this phase was obtained by cooling small droplets of the isotropic liquid and was identified by its characteristic schlieren texture. The fluid of each of the remaining homologues in this series could be supercooled to approximately 50°C below the melting point before crystallization occurred. Thus if these compounds are at all mesogenic, then the temperature at which liquid crystallinity is revealed, is certainly low. In contrast, the analogous disc–disc dimers, where the number of methylene units in the ether-linked spacer ranges from 8–12, are all reported to possess a discotic nematic phase whose clearing temperatures are well in excess of 100°C [5]. The transitional properties of the analogous rod–rod dimers are also well known, and here the nematic–isotropic transition temperatures are all in excess of 170°C [17]. It is apparent from these results that it is extremely difficult to pack the rod-like and disc-like units simultaneously so that their symmetry axes are either parallel to a common director or to two orthogonal directors as required for a biaxial nematic [11]. It is possible that this difficulty occurs because the flexible spacer linking the two mesogenic units is unable to decouple the unfavourable orientational correlations between them.

Table 2 also gives the transitional behaviour for binary mixtures of the 5DO*n*OCB series and TNF. All seven members gave a monotropic, viscous liquid crystal phase. The phase exhibited an indistinct sanded texture which only after annealing for several hours showed tiny, two and four point singularities (see figure 1 (*a*)); it also flashed when subjected to mechanical stress and so was assigned as a nematic phase. The equimolar composition was chosen because all of the contact preparations showed the existence of only a nematic phase at all temperatures and compositions. Moreover, optical microscopic observations indicated that the nematic–isotropic transition temperature peaked around the 50 : 50 mol % composition point. This is consistent with the observation, by optical microscopy, that this transition was sharp with no sign of coexisting nematic and isotropic phases. The occurrence of the maximum in T_{NI} for the equimolar mixture is compatible with some form of specific and favourable interaction between TNF and the disc-like moiety of the dimer. However, since the nematic–isotropic transition occurs below the melting point of the pure components, it is not possible to say with any certainty whether the nematic phase is chemically-induced or simply results from the eutectic behaviour of the mixture. Figure 2 shows the effect of the number of methylene units in the alkyl spacer on the transition temperatures for the equimolar mixtures. We see that there is no odd–even effect and that there is a gradual decrease in both T_{CI} and T_{NI} with increasing spacer length. This would seem to show that the spacer only plays a small role in determining T_{NI}, and suggests that the average geometric relationship between the rod-like and disc-like units does not vary significantly for odd membered or even membered spacers. This is in marked contrast to the behaviour found for the cyanobiphenyl rod–rod dimers, where the nematic–isotropic transition temperature exhibits a dramatic alternation with the parity of the number of methylene groups in the flexible spacer [17], partly as a result of the change in the geometric relation of the rod-like groups between the odd and even dimers [18]. We can quantify, at least pragmatically, the extent of the monotropic nature for this series by taking the difference ($T_{CI} - T_{NI}$) and scaling it with the mean of the crystal-isotropic and nematic-isotropic transition temperatures, i.e. ($T_{CI} + T_{NI}$)/2 (see figure 3). The results show that the monotropic nature of the transition increases with the length of the spacer, passes through a maximum for the nine spacer and then decreases again. It is difficult to rationalize this behaviour especially as the entropy of melting, which might influence the ability to supercool a sample, does not change significantly along the homologous series. Figure 4 shows the effect of the number of methylene units in the


(a)

(b)

Figure 1. (a) The sanded texture of the nematic phase of the equimolar mixture of 5DO6OCB and TNF formed on cooling from the isotropic phase; $T = 47°C$, magnification × 100. (b) The nematic phase texture of the equimolar mixture of DO6OCB and TNF on cooling from the isotropic phase; $T = 136°C$, magnification × 100.

alkyl spacer on the entropy change at the nematic-isotropic transition for the equimolar mixtures. For $n = 6$–10 the entropy change for this transition is very low ($\Delta S/R \approx 0{\cdot}1$) indicating the weakness of the transition and again is in marked contrast to the strong alternation found for the cyanobiphenyl rod-rod dimers [17]. In fact the small entropy of transition is similar to the discotic nematic-isotropic transition (0·1) of the hexakis(4-alkylphenylethynyl)benzenes [19] and the reported biaxial nematic-isotropic transition (0·1) of [(1,2,3,5,6-pentakis(4-pentylphenylethynyl)benzene-4′-oxy]nonane and α,ω-bis[(1,2,3,5,6-pentakis(4-pentylphenylethynyl)-benzene-4′-oxy]dodecane [5]. The equimolar mixtures of the undecyl and dodecyl homologues of the rod-disc dimer series show a larger entropy change ($\Delta S/R = 0{\cdot}2$ and 0·4, respectively) which might suggest a change in the molecular organization within the nematic phase. The argument for this is that the transitional entropy ($\Delta S/R$) for the columnar nematic phases formed from [1,2,3,5,6-pentakis(phenylethynyl) benzene-4′-oxy]nonane and -tridecane in their equimolar mixtures with TNF are 0·4 and 0·2 respectively; they are significantly larger than those for conventional discotic nematic phases [12]. The columnar nematic has the TNF and the disc-like moiety stacked alternately in short columns and it is the anisotropic interaction between these which is thought to be responsible for the nematic phase. Unfortunately the discotic and columnar nematic phases cannot be distinguished by miscibility studies as both phases are readily miscible with one another [20]. Indeed, due to the strong monotropic nature of the nematic phase in these systems, it did not prove possible to characterize further the structure of the nematic phase exhibited by the 5DO*n*OCB series since, during X-ray diffraction and deuterium NMR experiments, the sample crystallized. In consequence, because of the lack of information we can only speculate as to the structure of the nematic phase observed for this series. For the columnar nematic phase we can imagine the discs stacking into a column (separated by TNF) and to maximize the shape anisotropy of the molecular stack, the flexible spacers would have to adopt conformations which allow the rod-like groups to align with their long axes parallel to the column axis (see figure 5(*a*)). This organization of the rod-like units is analogous to that proposed for certain side chain liquid crystal polymers and termed the N_2 nematic phase; in contrast the N_1 phase has the rod-like mesogenic groups orthogonal rather than parallel to the polymer back bone [21]. For the structure sketched in figure 5(*a*) the nematic-isotropic transition temperature would exhibit little dependence on the length and parity of the spacer, except, of course, that a critical chain length is required to enable the rod-like unit to lie parallel to the columnar axis. It is for this reason, presumably, that columnar nematics only occur for the longest two spacers. It is equally difficult to be certain about the molecular organization within the discotic nematic phases formed with TNF by the rod-disc dimers with shorter spacers. A possible structure is one in which the dimers associate with the rod-like units more or less parallel, thus giving a lath-like object (see figure 5(*b*)). This might then form a nematic phase in which the TNF molecules could be relatively easily accommodated. The biaxiality of the combined unit would also be consistent with the low entropy change at the nematic-isotropic transition. However, the low stability of the nematic phase would make it extremely difficult to determine the symmetry of

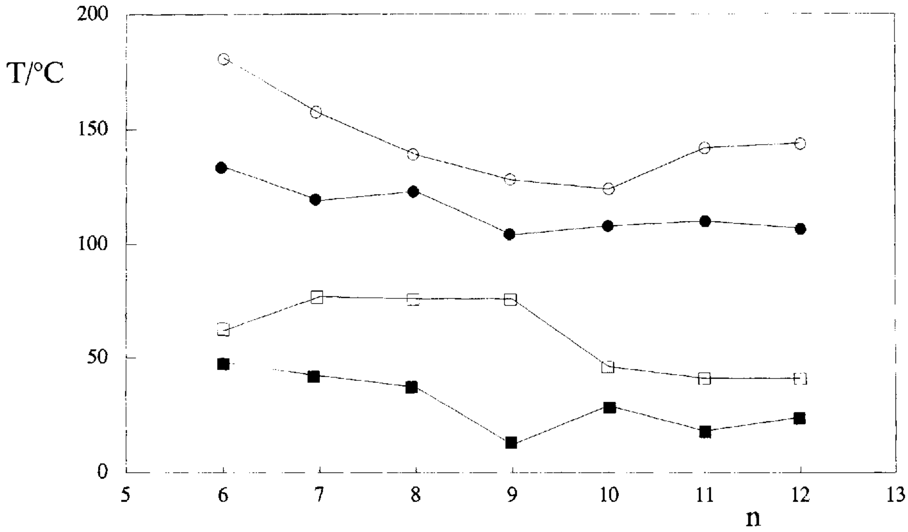


Figure 2. The influence of the number of methylene units in the alkyl spacer, *n*, on the transition temperatures for equimolar mixtures of TNF with the 5DO*n*OCB series (□, C–I; ■, N–I) and the DO*n*OCB series (○, C–I; ●, N–I).

the phase and the possiblity of a biaxial nematic cannot be ruled out.

3.2. *The DO*n*OCB series*

Table 3 lists the transition temperatures, enthalpy and entropy data for seven members of the DO*n*OCB series. As expected from the results for the 5DO*n*OCB series, none was liquid crystalline: the melting points for these compounds are higher than those of the analogous members of the 5DO*n*OCB series, since in the latter series the perimeter chains tend to dilute the disc–disc interactions and so disrupt the crystal packing. Contact preparations between members of the DO*n*OCB series and TNF gave a monotropic nematic phase which clearly showed two and four point singularities and which flashed when subjected to mechanical stress (see figure 1 (*b*)). It was also less viscous than the nematic phase exhibited by 5DO*n*OCB, presumably because of the significantly lower nematic–isotropic transition temperatures of this series compared with those of the DO*n*OCBs. For all of the homologues, the nematic–isotropic transition temperature was greatest for the equimolar composition, as for the 5DO*n*OCB series, which is in accord with the observation by optical

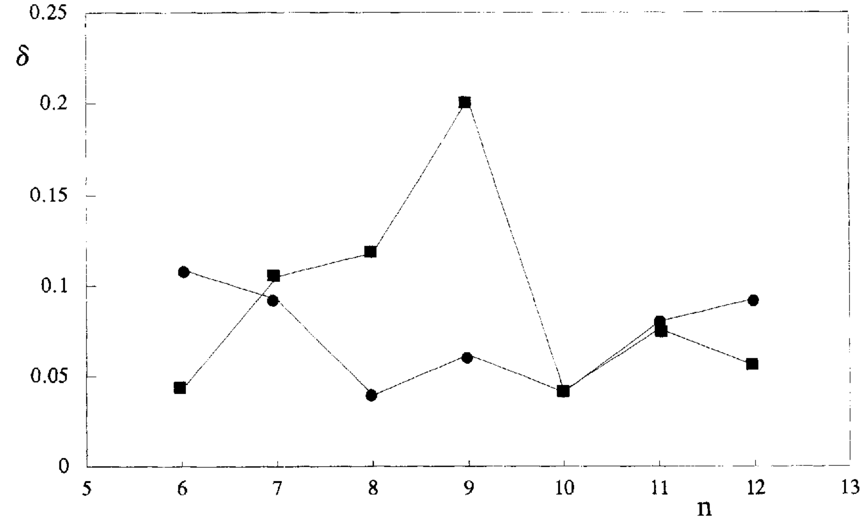


Figure 3. $T_{CI}-T_{NI}$ normalized by the average temperature $(T_{CI}+T_{NI})/2$, and denoted by δ, as a function of the number of methylene units in the flexible spacer, *n* for equimolar mixtures of TNF with the 5DO*n*OCB series (■) and the DO*n*OCB series (●).

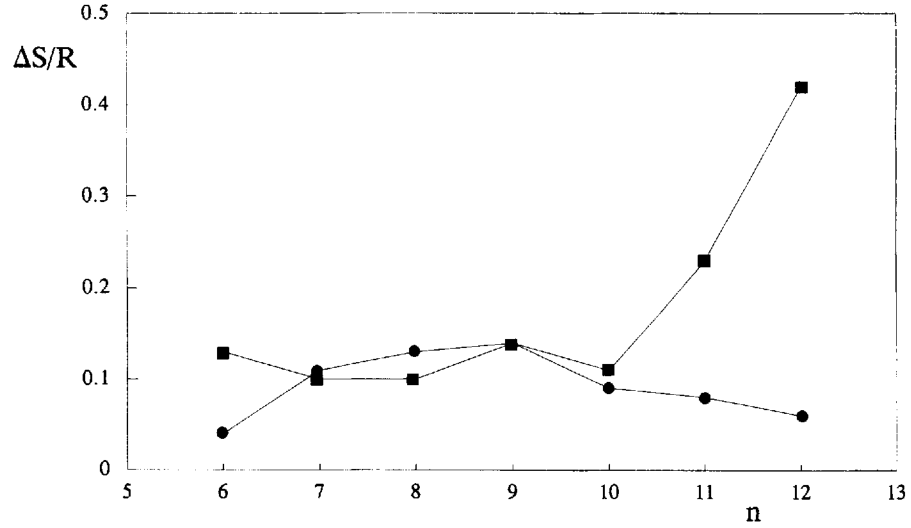


Figure 4. The influence of the number of methylene units in the alkyl spacer, *n* on the nematic–isotropic transitional entropy for equimolar mixtures of TNF with the 5DO*n*OCB series (■) and the DO*n*OCB series (●).

microscopy that the transition was sharp with no indication of coexisting nematic and isotropic phases. Again this is a likely consequence of the disc–TNF interactions which help to create the nematic phase, although we cannot be certain because this transition temperature is below the melting points of the individual components.

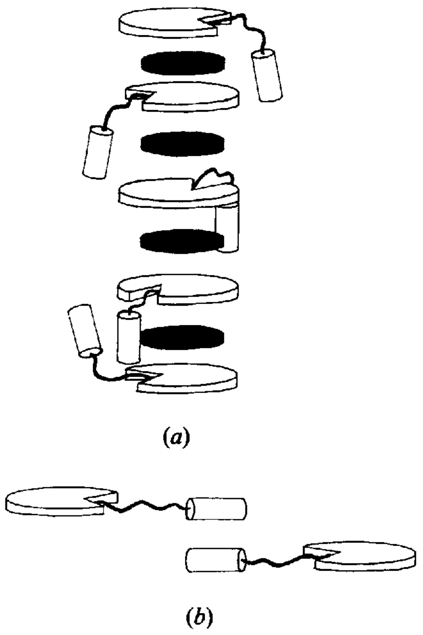


Figure 5. Schematic representation of the possible *local* molecular organization in (*a*) a columnar nematic and (*b*) a discotic nematic phase for the equimolar mixtures of the 5DO*n*OCB and DO*n*OCB series with TNF. The shaded discs in (*a*) denote TNF molecules; these are not included in (*b*).

Table 3 also gives the transitional data for the equimolar mixtures of DO*n*OCB and TNF. As for the 5DO*n*OCB and TNF mixtures, all of the nematic phases were monotropic. However, the nematic–isotropic transition temperatures of the DO*n*OCB and TNF mixtures are all much higher than their 5DO*n*OCB counterparts, as expected. For the 5DO*n*OCB series, the perimeter pentyl chains help to lower the clearing temperatures by increasing the average separation between the mesogenic groups and so reducing the anisotropic interactions. Figure 2 shows the influence of the number of methylene units in the spacer, *n*, on the transition temperatures of equimolar mixtures of DO*n*OCB and TNF. There is very little evidence of an odd–even effect for the nematic–isotropic transition temperatures of this series, as was the case for the 5DO*n*OCB series. Thus, again it appears that the spacer has little influence on the nematic–isotropic transition temperature; this suggests that the geometric relationship between the rod-like and disc-like units does not vary significantly between odd membered and even membered spacers. As for the 5DO*n*OCB series, we can quantify the extent of the monotropic nature of these compounds (see figure 3). Now the monotropic character decreases slightly as the spacer length increases, but with no hint of a maximum in the middle of the series; again this behaviour is difficult to understand. Figure 4 shows the effect of the number of methylene units in the spacer, *n*, on the nematic–isotropic entropy change for the equimolar mixtures of DO*n*OCB and TNF. The nematic–isotropic transitional entropies are all very small, with $\Delta S/R$ being approximately 0·1, and are characteristic of a discotic nematic phase or indeed a nematic composed of relatively biaxial units such as the

Table 3. The transition temperatures, enthalpies and entropies of the DO*n*OCB series and their equimolar mixtures with TNF.

	DO*n*OCB			DO*n*OCB + TNF (50 : 50 mol%)					
n	T_{CI}/°C	ΔH_{CI}/kJ mol^{-1}	ΔS_{CI}/R	T_{CI}/°C	T_{NI}/°C	ΔH_{CI}/kJ mol^{-1}	ΔH_{NI}/kJ mol^{-1}	ΔS_{CI}/R	ΔS_{NI}/R
6	180	70·3	18·71	181	(134)	35·9	(0·1)	9·28	(0·04)
7	179	48·0	12·86	157	(119)	19·3	(0·4)	5·40	(0·11)
8	150	42·3	12·03	139	(123)	22·8	(0·4)	6·66	(0·13)
9	148	30·5	8·79	128	(104)	25·4	(0·4)	8·80	(0·14)
10	122	23·8	7·23	124	(108)	12·6	(0·3)	4·01	(0·09)
11	126	34·7	10·51	142	(110)	36·0	(0·3)	10·51	(0·08)
12	91	11·9	3·93	144	(107)	36·0	(0·2)	10·45	(0·06)

Parentheses indicate a monotropic transition.

associated pair of rod–disc dimers in figure 5 (*b*). They are, however, at least a factor of two smaller than those for the columnar nematic–isotropic transition found for equimolar mixtures of TNF with the corresponding monomer in which the cyanobiphenyl group in the rod-disc dimer is replaced by a hydrogen [12]. Unfortunately, because of the monotropic nature of the nematic phase exhibited by these compounds, it was not possible to study them using other techniques, and so we do not have a clear picture of the molecular organization within this nematic phase. In consequence, the symmetry of this nematic phase formed by binary mixtures of the rod–disc dimers, DO*n*OCB, with TNF remains an open question.

4. Conclusions

We have synthesized two series of non-symmetric dimers composed of rod-like and disc-like mesogenic units linked via a flexible spacer. The 5DO*n*OCB members were not liquid crystalline, but when mixed with TNF, each gave a monotropic liquid crystalline phase which had a very indistinct optical texture. However, it flashed when stressed mechanically and so was identified as a nematic phase. Based on the very low clearing transitional entropy changes for the $n = 6$–10 homologues of this series, the liquid crystal phase appears to be a discotic nematic. The $n = 11$ and 12 homologues also gave nematic phases and had, respectively, entropies of transition two and four orders of magnitude higher than those of the other homologues. This suggests that these phases were columnar nematics, but this possibility could not be confirmed because of their extreme monotropic nature, which prevented structural studies. Members of the DO*n*OCB series were, as expected, not liquid crystalline. When mixed with TNF they exhibited a monotropic nematic phase which was characterized by a well-defined schlieren texture. The nematic–isotropic transitional entropies were all similar to those of the $n = 6$–10 homologues of the 5DO*n*OCB series and so the nematic phase was assigned as being a discotic nematic. Again the monotropic nature of the nematic phase made it impossible to investigate the molecular organization within this phase in any detail and certainly prevents a reliable determination of the phase symmetry.

The prediction that a compound combining rod-like and disc-like character should yield a biaxial nematic phase still remains to be proven.

We are grateful to the Science and Engineering Research Council for the award of a CASE Research Studentship with GEC to Dr I. D. Fletcher. We also wish to acknowledge valuable discussions with Professor Dr K. Praefcke concerning discotic liquid crystals and chemically induced phases made possible by a NATO Collaborative Research Grant.

References

[1] Freiser, M. J., 1970, *Phys. Rev. Lett.*, **24**, 1041.

[2] Malthête, J., Liebert, L., Levelut, A.-M., and Galerne, Y., 1986, *C. r. hebd. Séanc Acad. Sci. Paris II*, **303**, 1073.

[3] Shenouda, I. G., Shi, Y., and Neubert, M. E., 1994, *Molec. Crystals liq. Crystals* (in the press).

[4] Chandrasekhar, S., Sadashiva, B. K., Ratna, B. R., and Raja, N. V., 1988, *Pramana*, **30**, L491 Chandrasekhar, S., Ratna, B. R., Sadashiva, B. K., and Raja, N. V., 1988, *Molec. Crystals liq. Crystals*, **165**, 123.

[5] Praefcke, K., Kohne, B., Gündogan, B., Singer, D., Demus, D., Diele, D., Pelzl, G., and Bakowsky, U., 1991, *Molec. Crystals liq. Crystals*, **198**, 393.

[6] Praefcke, K., Kohne, B., Gündogan, B., Demus, D., Diele, D., and Pelzl, G., 1990, *Molec. Crystals liq. Crystals*, **165**, 123.

[7] Yu, L. J., and Saupe, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.

[8] Fan, S. M., Fletcher, I. D., Gündogan, B., Heaton, N. J., Kothe, G. Luckhurst, G. R., and Praefcke, K., 1993, *Chem. Phys. Lett.*, **204**, 517.

[9] Alben, R., 1973, *J. chem.*, **59**, 4299.

[10] Pratibhar, R., and Madhusudana, N. V., 1985, *Molec. Crystals liq. Crystals Lett.*, **1**, 111.

[11] Hashim, R., Luckhurst, G. R., Prata, F., and Romano, S., 1993, *Liq. Crystals*, **15**, 283.

[12] Praefcke, K., Singer, D., Kohne, B., Ebert, M., Liebman, A., and Wendorff, J. H., 1991, *Liq. Crystals*, **10**, 147.

[13] Keller, P., and Liebert, L., 1978, *Sol. St. Phys., Suppl.*, **14,** 19.

[14] Praefcke, K., Kohne, B., Gutbier, K., Johnen, N., and Singer, D., 1989, *Liq. Crystals*, **5,** 233.

[15] Attard, G. S., Date, R. W., Imrie, C. T., Luckhurst, G. R., Roskilly, S. J., Seddon, J. M., and Taylor, L., 1994, *Liq. Crystals*, **16,** 529.

[16] Singer, D., Institut für Organische Chemie, Technische Universität Berlin (private communication).

[17] Emsley, J. W., Luckhurst, G. R., Shilstone, G. N., and Sage, I., 1984, *Molec. Crystals liq. Crystals Lett.*, **102,** 223.

[18] Ferrarini, A., Luckhurst, G. R., Nordio, P. L., and Roskilly, S. J., 1993, *Chem. Phys. Lett*, **214,** 409.

[19] Praefcke, K., Kohne, B., and Singer, D., 1990, *Angew. Chem. Int. Ed. Engl.*, **29,** 177.

[20] Singer, D., Liebmann, A., Praefcke, K., and Wendorff, J. H., 1993, *Liq. Crystals*, **14,** 785.

[21] Wang, X. J., and Warner, M., 1987, *J. Phys.* A, **20,** 713.