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Cyano substituted triphenylene-based discotic mesogens

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Cyano groups have been introduced into alkoxytriphenylene-based mesogens by bromination followed by treatment with copper(I) cyanide. The introduction of cyano substitutents enhances the mesophases ranges.

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1. Introduction

Some of the most important calamitic liquid crystal materials used in optoelectronic devices are cyano compounds. The cyano group introduces a permanent dipole into the molecule allowing the nematic phase to be switched. It also allows a number of functional group interchange reactions to be exploited, opening up further variations in the molecular structure. This paper describes the synthesis of cyano substituted discotic liquid crystal materials. Previous studies had shown that the introduction of α-nitro [1], α-halogeno [2, 3], and α-alkoxy [4] substitutents into 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6) [5] distorts the ring from its normal planar geometry but, at the same time, the mesophase range is enhanced (see the table). We now show that the introduction of α- and β-cyano groups also enhances the mesophase range.

2. Results and discussion

In principle the cyanation could have been achieved directly using cyanogen bromide [6], but we have used an indirect method in which a bromine is first introduced and then displaced using copper(I) cyanide [7]. The synthesis of the monocyano derivative is shown in scheme 1 and that of a dicyano derivative in scheme 2. It should be noted that the synthesis of 2-bromo-3,6,7,10,11-pentahexyloxytriphenylene shown in scheme 1, involving the molybdenum pentachloride [8] mediated coupling reaction, is considerably more efficient than that previously published [9].

2-Bromo-3,6,7,10,11-pentahexyloxytriphenylene and 2-cyano-3,6,7,10,11-pentahexyloxytriphenylene both form columnar liquid crystal phases as detailed in the table. Compared with the symmetrical HAT6, the mesophase has been greatly stabilized and its range enhanced. Low

Table. Phase behaviour of the principle compounds discussed.

	Phase transition	
Compound	Temperature °C (enthlapy/J g^{-1})	Reference
2,3,6,7,10,11-Hexahexyloxytriphenylene	Cr 67 Col 100 I	[5]
1-Nitro-2,3,6,7,10,11-hexahexyloxytriphenylene	<r.t. Col 136 I	[1]
1-Fluoro-2,3,6,7,10,11-hexahexyloxytriphenylene	Cr 39 Col 116 I	[2]
1-Chloro-2,3,6,7,10,11-hexahexyloxytriphenylene	Cr 37 Col 98 I	[2]
1-Bromo-2,3,6,7,10,11-hexahexyloxytriphenylene	Cr 37 Col 83 I	[2]
2-Bromo-3,6,7,10,11-pentahexyloxytriphenylene	Cr 54 (44) Col 142 (8) I I 144 (– 8) Col<r.t.	this paper
2-Cyano-3,6,7,10,11-pentahexyloxytriphenylene	Cr$_1$ 75 (9) Cr$_2$ 93 (38) Col 214 (13) I I 214 (– 12) Col<r.t.	this paper
1,8-Dicyano-2,3,6,710,11-hexahexyloxytriphenylene	<r.t. Col 236.9 (14) I I 236.1 (– 14) Col<r.t.	this paper

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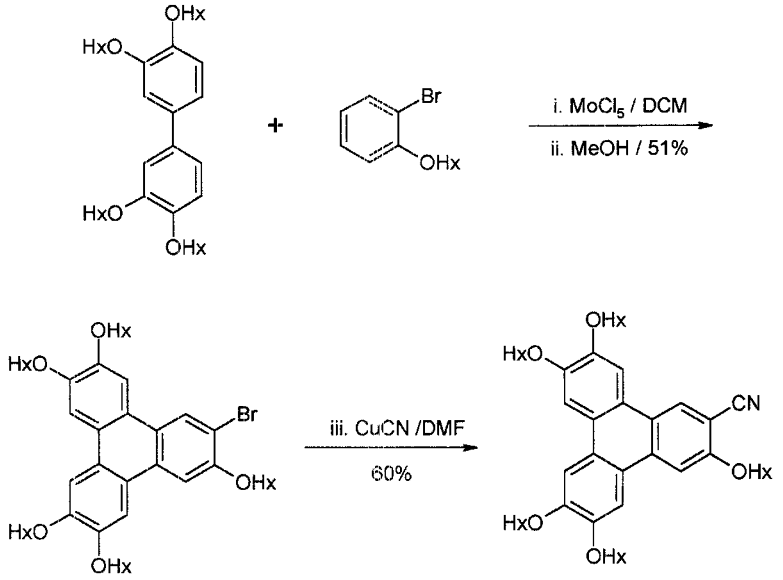
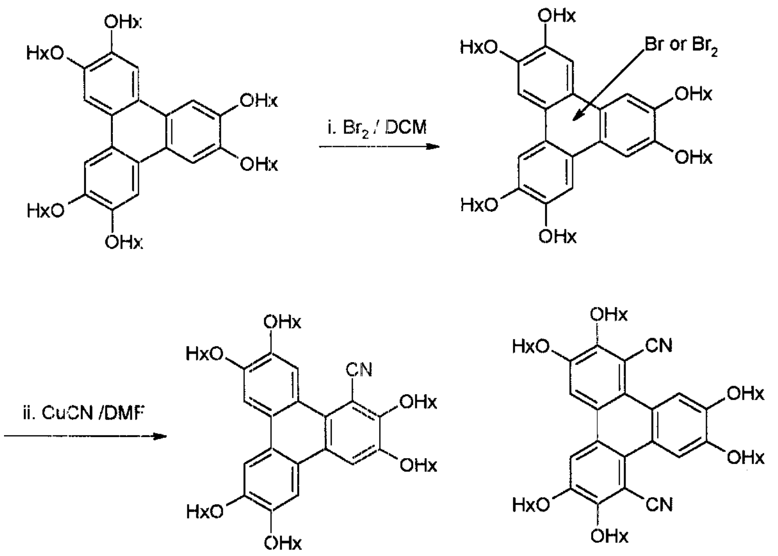


Scheme 1. Synthesis of 2-cyano-3,6,7,10,11-pentahexyloxytriphenylene.



Scheme 2. Synthesis of 1,8-dicyano-2,3,6,7,10,11-hexahexyloxytriphenylene. The 1-cyano derivative could not be isolated in a completely pure state.

angle X-ray diffraction measurements at 82 and 150°C showed two diffraction peaks (corresponding to 25.5 and 18.5 Å) for the Cr_2 phase of the cyano discogen at 82°C and only one diffraction peak (corresponding to 18.1 Å) at 150°C in the hexagonal columnar phase. This is close to the value found for pentahexloxytriphenylene.

1,8-Dicyano-2,3,6,710,11-hexahexyloxytriphenylene also forms a hexagonal columnar phase and its mesogenic behaviour is detailed in the table. Relative to HAT6, the clearing temperature is higher and the range of the mesophase has been enhanced. Low angle X-ray diffraction measurements at 100 and 200°C show that there is only one diffraction peak corresponding to 18.7 Å, which is close to that of HAT6 [10].

Whereas the structure of the mono-cyano derivative follows unambiguously from the method of synthesis, spectroscopic and analytical data, the dicyano compound was obtained from a mixture of the mono- and di-bromides. Determination of the substitution pattern in the nitrile is not straightforward. The ^{1}H NMR spectrum showed two hydrogen singlets showing it to possess a plane of symmetry. Of the three symmetrical structures (scheme 3), the third can be discounted because of the strong steric clash that this would entail

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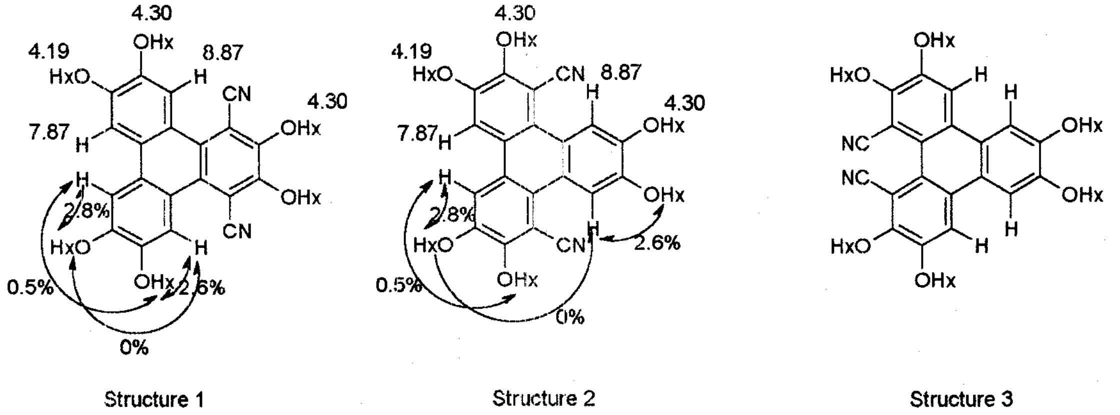

Scheme 3. Putative structures and the corresponding ^{1}H NMR chemical shift and NOE assignments required for the dicyano product (see text).

and the observation of a highly deshielded proton at 8.87δ in the ^{1}H NMR spectrum [1–3].

Structure 2 is favoured on the basis of the chemical shifts of the aromatic hydrogens and the α-methylenes of the side chains (comparing the unsubstituted, monocyano and dicyano compounds) but more clearly by NOE studies. The measured NOE effects between the aryl and next-but-one alkoxy groups would be expected to be equal if structure 1 were correct. They are not and, whereas the effect is small, this clearly supports structure 2.

Structure 2 was finally confirmed on the basis of 'J-resolved' ^{1}H NMR experiments (270 MHz) on both mononitrile and dinitrile. The spectrum of the mononitrile (see the figure) clearly shows '*para*' couplings to four of the signals. Under equivalent conditions 'J-resolved' ^{1}H NMR on the dicyanide showed two

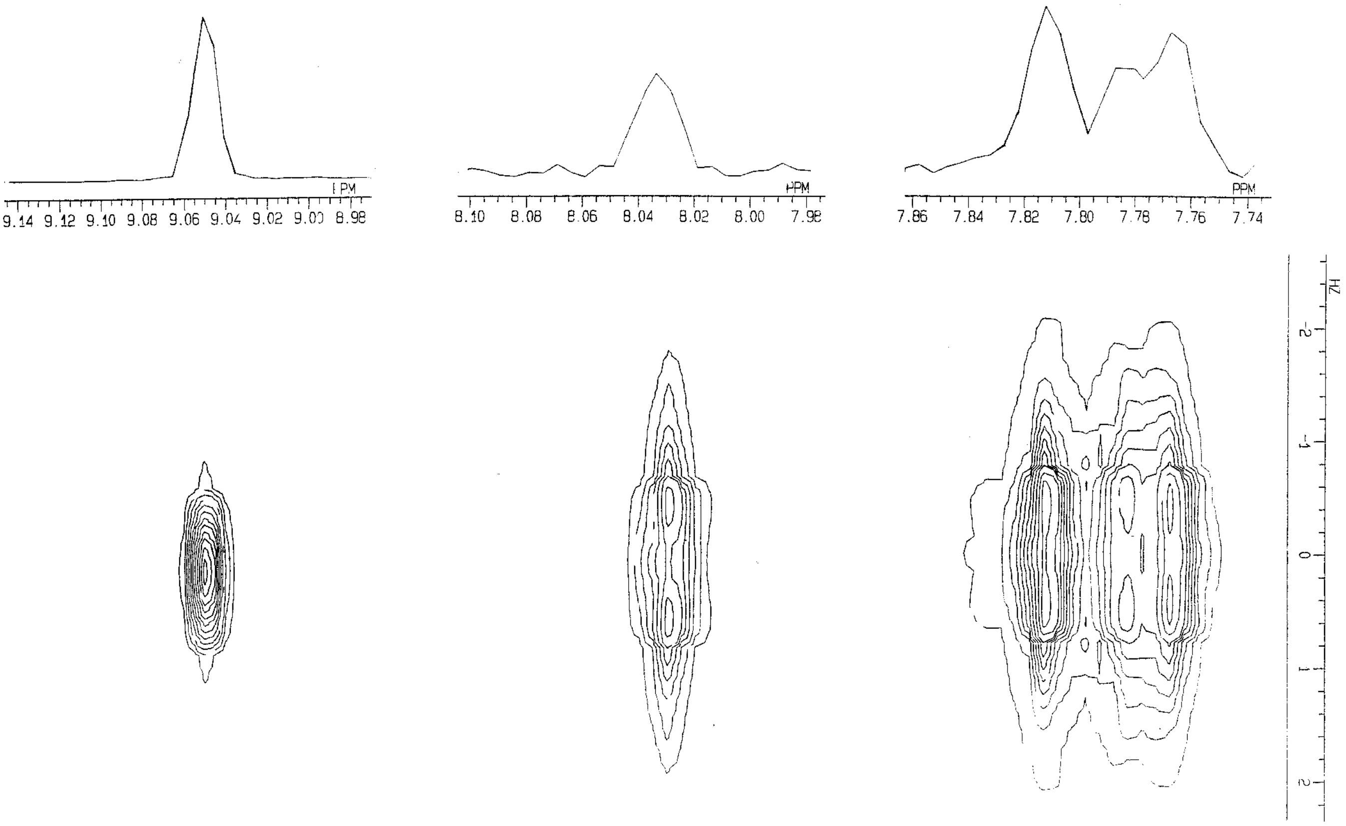

Figure. 'J-resolved' ^{1}H NMR spectra of the aromatic protons of 1-cyano-2,3,6,7,10,11-hexahexyloxytriphenylene.

singlets. ('*para*' coupled doublets would have been observed if structure 1 were correct).

3. Conclusion

Cyano groups can be conveniently introduced into triphenylene-based mesogens by bromination and treatment of the products with copper cyanide. The introduction of such substitutents enhances the mesophases ranges.

4. Experimental

4.1. *2-Bromo-3,6,7,10,11-pentahexyloxytriphenylene*

Molybdenum (V) chloride [8] (6.55 g, 24 mmol) was added to a stirred mixture of 3,3′,4,4′-tetrahexyloxybiphenyl [11] (4.45 g, 8.0 mmol) and 2-bromo-1-hexyloxybenzene (4.11 g, 16 mmol) in dichloromethane (50 ml) under nitrogen at room temperature. After the reaction was complete (*c.* $\frac{1}{2}$ h), the solution was carefully poured into methanol (50 ml) and water (50 ml) added. The organic layer was separated, washed with water (100 ml), dried with magnesium sulphate, filtered, concentrated *in vacuo* and purified by column chromatography (on silica eluting with dichloromethane : petroleum ether 1 : 1). Recrystallization from ethanol gave white crystals (3.30 g, 51%, Cr → Col 54, Col → I 142°C). Elemental analysis: C 71.25, H 8.9, Br 9.8; $C_{48}H_{71}BrO_5$ requires C 71.36, H 8.85, Br 9.89%. MS: *m/z* (EI), 808 ($[M]^+$, 100%) and 806 ($[M]^+$, 91%). ^1H NMR: δ_H ($CDCl_3$) 0.93 (15H, 2 × t, $J = 6.9$ Hz, $O(CH_2)_5CH_3$), 1.20–1.70 (30H, m, $OCH_2CH_2(CH_2)_3$), 1.94 (10H, m, OCH_2CH_2), 4.23 (10H, 2 × t, $J = 6.5$ Hz, OCH_2), 7.78 (1H, s, *ArH*), 7.80 (3H, s, *ArH*), 7.85 (1H, s, *ArH*), 8.59 (1H, s, *ArH*).

4.2. *2-Cyano-3,6,7,10,11-pentahexyloxytriphenylene*

A mixture of 2-bromo-3,6,7,10,11-pentahexyloxytriphenylene (3.14 g, 4.0 mmol) and copper(I) cyanide (0.72 g, 8.0 mmol) in dimethylformamide (50 ml) was heated under reflux in a nitrogen atmosphere for 8 h. After the reaction was complete, the mixture was cooled to room temperature, poured into 1M aqueous ammonia (200 ml), and organic product extracted with dichloromethane (2 × 50 ml). The extracts were washed with water until colourless, dried with magnesium sulphate, filtered and concentrated *in vacuo* to obtain the crude product. This was purified by column chromatography (on silica eluting with dichloromethane : petroleum ether 1 : 1) and recrystallized from ethanol to give white crystals (1.76 g, 60%, $Cr_1 \rightarrow Cr_2$ 75, $Cr_2 \rightarrow$ Col 93, Col → I 214°C). Elemental analysis: C 78.15, H 9.5, N 1.85; $C_{49}H_{71}NO_5$ requires C 78.05, H 9.48, N 1.86%. MS: *m/z* (EI), 753 ($[M]^+$, 100%). ^1H NMR: δ_H ($CDCl_3$) 0.94 (15H, t, $J = 6.9$ Hz, $O(CH_2)_5CH_3$), 1.30–1.70 (30H, m, $OCH_2CH_2(CH_2)_3$), 1.94 (10H, m, OCH_2CH_2), 4.25 (10H, 2 × t, $J = 6.4$ Hz, OCH_2), 7.78 (4H, s, *ArH*), 7.82 (1H, s, *ArH*), 8.64 (1H, s, *ArH*).

4.3. *1,8-Dicyano-2,3,6,7,10,11-hexahexyloxytriphenylene*

Bromine (2.90 g, 18 mmol) in dry dichloromethane (50 ml) was added dropwise over 2 h to a vigorously stirred solution of 2,3,6,7,10,11-hexahexyloxytriphenylene [5] (10 g, 12 mmol) in dry dichloromethane (350 ml) under an atmosphere of nitrogen. After the addition, the mixture was stirred overnight. Water (50 ml) was added, the organic phase separated, dried with magnesium sulphate, filtered and concentrated *in vacuo* to give the mixture of bromo-substituted 2,3,6,7,10,11-hexahexyloxytriphenylenes as a yellow oil (7.5 g). This mixture and copper(I) cyanide (2.0 g, 8 mmol) in dimethylformamide (50 ml) were heated under reflux for 8 h. After the reaction was complete, the mixture was cooled to room temperature, poured into 1M aqueous ammonia (200 ml), and organic product extracted with dichloromethane (2 × 100 ml). The organic extracts were washed with water until colourless, dried with magnesium sulphate and concentrated *in vacuo* to give the crude product. This was purified by column chromatography (on silica eluting with dichloromethane : petroleum ether 1 : 1) and recrystallized first from cold hexane, then from acetone at room temperature to give recovered 2,3,6,7,10,11-hexahexyloxytriphenylene and its mono- and di-nitrile derivatives.

For *1,8-dicyano-2,3,6,7,10,11-hexahexyloxytriphenylene* (<r.t. Col → I 236.9°C). Elemental analysis: C 76.2, H 9.35, N 3.25; $C_{56}H_{82}N_2O_6$ requires C 76.50, H 9.40, N 3.19%. MS: *m/z* (EI), 878 ($[M]^+$, 100%). ^1H NMR: δ_H ($CDCl_3$) 0.92 (18H, 2 × t, $J = 6.7$ Hz, $O(CH_2)_5CH_3$), 1.30–1.70 (36H, m, $OCH_2CH_2(CH_2)_3$), 1.94 (12H, m, OCH_2CH_2), 4.21 (4H, t, $J = 6.4$ Hz, OCH_2), 4.31 (8H, t, $J = 6.6$ Hz, OCH_2), 7.92 (2H, s, *ArH*), 8.90 (2H, s, *ArH*).

For *1-cyano-2,3,6,7,10,11-hexahexyloxytriphenylene* ^1H NMR: δ_H ($CDCl_3$) 0.92 (18H, 2 × t, $J = 6.7$ Hz, $O(CH_2)_5CH_3$), 1.30–1.70 (36H, m, $OCH_2CH_2(CH_2)_3$), 1.94 (12H, m, OCH_2CH_2), 4.21 (10H, t, $J = 6.4$ Hz, OCH_2), 4.31 (2H, t, $J = 6.6$ Hz, OCH_2), 7.787 (1H, s, *ArH*), 7.794 (1H, s, *ArH*), 7.82 (1H, s, *ArH*), 8.05 (1H, s, *ArH*), 8.05 (1H, s, *ArH*). This material was contaminated with traces of starting material which we were unable to remove.

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