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Electrophilic aromatic substitution in triphenylene discotics: Synthesis of alkoxynitrotriphenylenes

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Functionalization of triphenylene-based discotic liquid crystals by direct nitration of hexaalkoxytriphenylene has very recently been reported to produce exclusively the mononitrohexaalkoxytriphenylene. We have found that nitration of such discotics is not restricted to only one ring of triphenylene, but all the three rings can be nitrated successively to produce mononitro-, dinitro- and trinitro-hexaalkoxytriphenylenes. All the mononitro derivatives show a very broad mesophase range. While the dinitrohexabutyloxytriphenylene is non-liquid crystalline, its higher homologues are room temperature liquid crystals. Photomicroscopic pictures of these liquid crystalline materials show classical textures of an ordered hexagonal columnar phase. X-ray diffraction studies of two representative compounds, **4a** and **4b**, confirmed the above conclusions. None of the trinitro derivatives are liquid crystalline. Nitrotriphenylenes are valuable precursors to several other triphenylene derivatives like amino, acyl, alkylamino, diazo, etc. Mononitration of 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylenes gives the 1-nitro-2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylenes. These double functionalized triphenylene derivatives are extremely important precursors as the functional group such as nitro, amino, azo, etc. can be utilized to modify the electronic nature of the core and at the same time the hydroxy functional group may be converted to a polymerizable group. Thus, processable oligomers and polymers can be synthesized.

1. Introduction

Discotic liquid crystals [1, 2] are generally formed by flat or nearly flat molecular cores surrounded by three or more long chain substituents. Triphenylene represents one of the most important core forming discotic liquid crystals. Several hexaalkoxytriphenylene discotic liquid crystals are extensively studied for their one-dimensional conducting [3], photoconducting [4] and one-dimensional energy transfer [5] properties. The columnar phase of hexaalkoxytriphenylene can be made conducting by doping with electron acceptors. The conductivity increases by about six orders of magnitude in an aligned sample of hexahexyloxytriphenylene doped with 1 mol% of electron acceptor $AlCl_3$ [3]. The hexagonal ordered phase (Col_h) of triphenylene ethers is well suited for the study of one-dimensional energy transfer [5]. Photoinduced charge carrier mobility (hole mobility) of the order of 10^{-3}, 10^{-2} and 10^{-1} $cm^2 V^{-1} s^{-1}$ has been reported in the Col_{ho} phase of hexapentyloxytriphenylene (H5TP) [4*a*], the discotic plastic phase (Col_p) of hexabutyloxytriphenylene (H4TP) [4*e*] and the helical phase of hexahexylthiotriphenylene [4*d*] respectively.

For liquid crystal device purposes, besides molecular stability, the supramolecular structure of the desired mesophase must be thermodynamically stable over a broad temperature range above and below room temperature and the material should have easy processability. Different functionalized triphenylene derivatives have recently been prepared in many laboratories in order to tailor the mesophase properties and processability. Mono- and di-functional triphenylenes were prepared and converted to side chain and main chain polymers by Ringsdorf and co-workers [6]. Selective ether cleavage of hexaalkoxytriphenylene resulted in the synthesis of mono-, di-, and

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tri-functionalized triphenylenes in high yields [7]. We have recently reported the synthesis of functionalized triphenylene derivatives using $MoCl_5$ [8] and catechol boron bromide [9]. Triphenylene dimers and oligomers have been prepared to stabilize the mesophase [10]. The stabilization of the columnar phase was also achieved by forming charge transfer complexes [11] and by inserting oxygen atoms in the side chain, the so called β-oxygen effect [12]. In another approach, a glass-forming low molar mass triphenylene discotic was prepared by replacing one of the ether chains of hexaalkoxytriphenylene by an ester grouping [13] or by a fluoroalkylated chain [14].

Most of the triphenylene discotic liquid crystals are colourless, poorly fluorescent materials and thus their use in many applications is limited. In order to induce molecular dipoles, colour etc., Boden *et al.* have recently nitrated the triphenylene discotics at the 1-position [15]. In an effort to enhance fluorescence as well as the mesogenicity of triphenylene discotic LCs, we have synthesized a number of new monofunctionalized triphenylene and mixed tail triphenylene discotics bearing conjugative electron withdrawing substituents attached directly to the triphenylene core [10, 16]. Direct nitration of triphenylene discotics is an attractive approach to produce functionalized triphenylene derivatives having lateral dipoles moment, colour, etc. Electrophilic aromatic substitution in unsubstituted triphenylene is directed by steric and electronic effects. Substitution at the β- or 2-position is favoured compared with the α or 1-position, presumably owing to a steric hindrance effect [17]. However, the electronic effect plays a major role in the nitration of triphenylene and results in a mixture of 1-nitro and 2-nitro triphenylene [17]. During the course of low symmetry, fluorescent triphenylene synthesis, when we nitrated pentapentyloxytriphenylene, nitration occurred preferentially in the sterically hindered α-position (scheme 1) [16]. Evidently electronic effects dominate in the nitration of alkoxy triphenylenes. This prompted us to examine the nitration of triphenylene discotics more carefully. In a preliminary communication [18] we have recently reported the synthesis of mono-, di- and trinitrohexabutyloxytriphenylenes. Here we wish to report the preparation, characterization and X-ray studies of various nitrotriphenylenes and their derivatives in detail.

2. Experimental

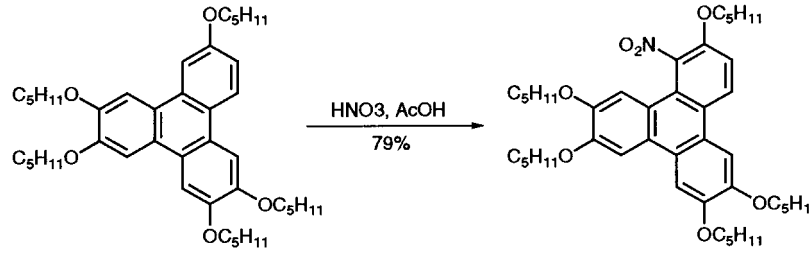
2.1. *General information*

Chemicals and solvents (AR quality) were obtained from E. Merck and used as such without any purification. Column chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh) and neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). Mass spectra were recorded on a Finnigan Mat 90 spectrometer in FAB+ mode using *m*-nitrobenzylalcohol (NBA) matrix. NMR spectra were recorded on a 200 or 250 MHz Bruker Ac 250 NMR spectrometer in $CDCl_3$. All chemical shifts are reported in δ units downfield from Me_4Si. The synthesis of various triphenylene derivatives is outlined in schemes 2 and 3.

2.2. *Synthesis*

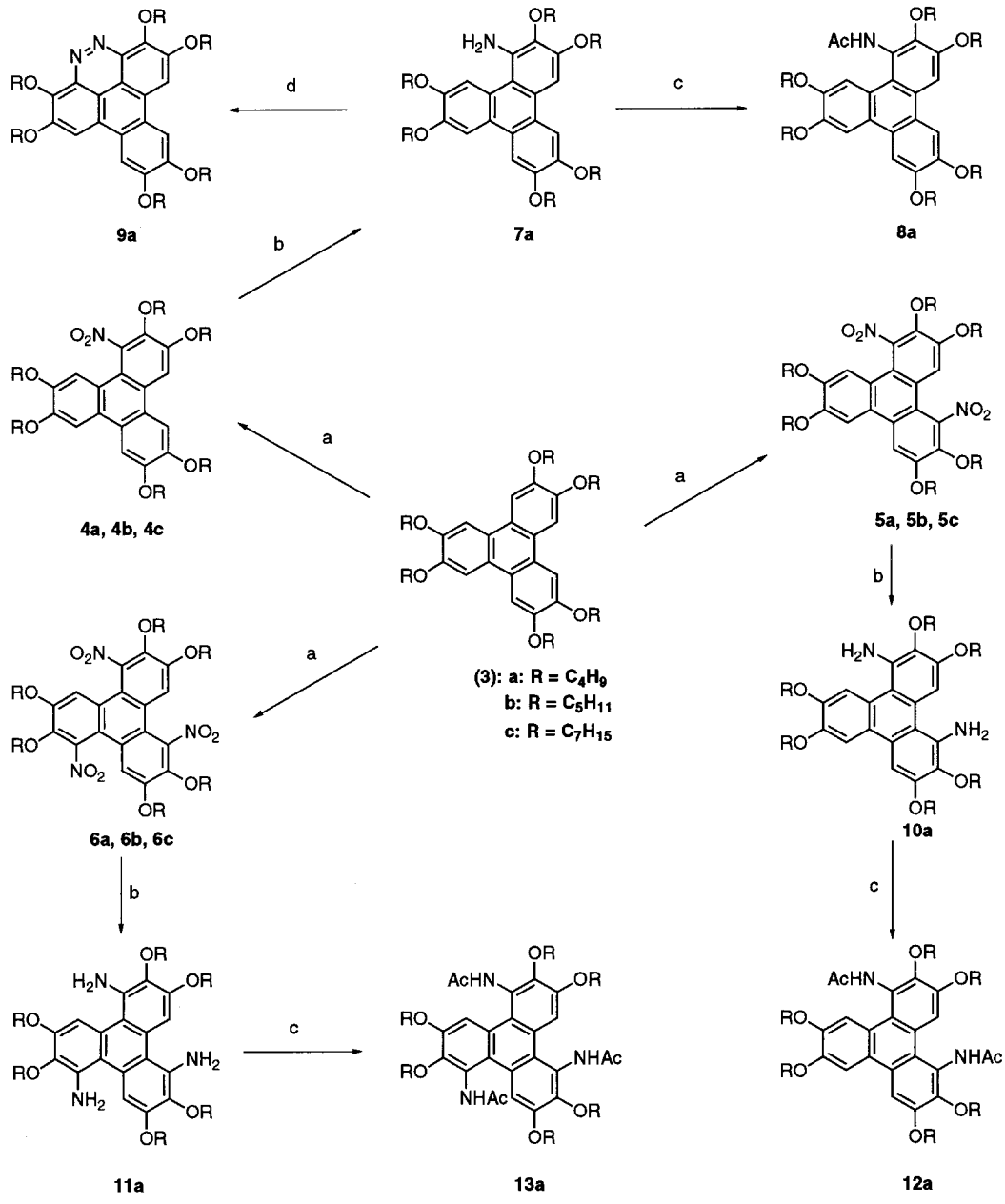
2.2.1. *2,3,6,7,10,11-Hexabutyloxytriphenylen e (**3a**) and 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene (**14a**)*

Compounds **3a** and **14a** were prepared in a single reaction by the modified method of Boden *et al.* [15]. 1,2-dibutyloxybenzene (22.2 g, 0.1 mol) was dissolved in 125 ml of CH_2Cl_2 containing 2% conc. H_2SO_4. To this, anhydrous $FeCl_3$ was added (48.6 g, 0.3 mol) in portions and the reaction mixture was stirred at room temperature for 30 min. It was then poured into cold MeOH (250 ml). The precipitate was filtered off and to the filtrate about 1 litre of H_2O was added; it was then extracted with CH_2Cl_2, and the solvent removed under vacuum. The resultant solid and the precipitate were combined and repeatedly chromatographed over neutral alumina. Elution with 10–20% CH_2Cl_2 in hexane gave 14 g of H4TP (**3a**). Elution with 40–50% CH_2Cl_2 afforded 3.5 g of monohydroxy-H4TP (**14a**). These compounds were also prepared using $MoCl_5$ and catechol boron bromide as reported by us recently [8, 9, 18].



Scheme 1. Nitration of pentaalkoxytriphenylene.

1 **2**



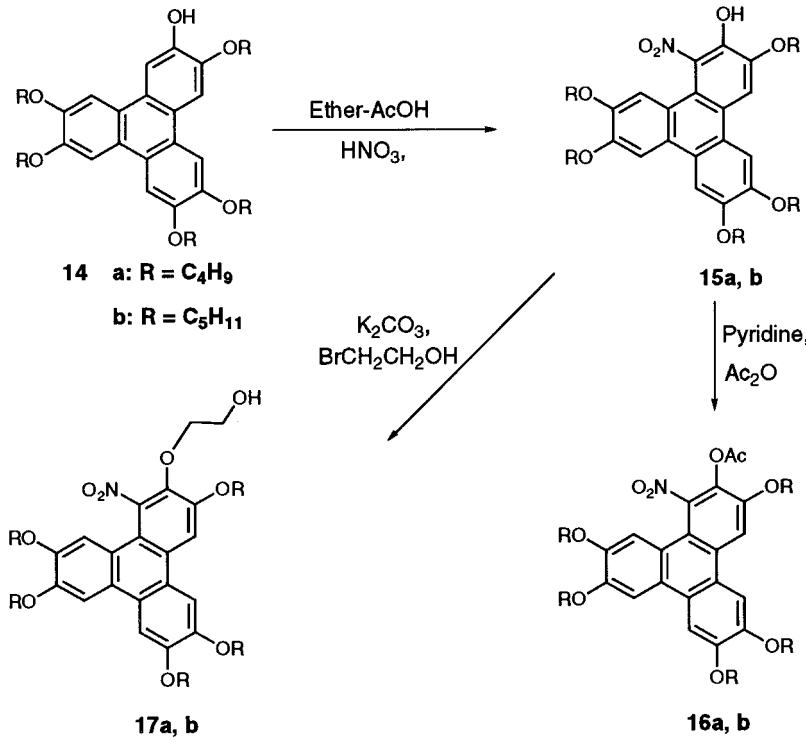
Scheme 2. Nitration of hexaalkoxytriphenylenes. *Reagents and conditions:* a, CH_2Cl_2–CH_3NO_2, HNO_3, r.t.; b, THF–MeOH, $NiCl_2.6H_2O$, $NaBH_4$, r.t., 0.5 h; c, Pyridine, Ac_2O; d, CH_2Cl_2–AcOH, $NaNO_2$.

2.2.2. *2,3,6,7,10,11-Hexapentyloxytriphenylen e (**3b**), 2,3,6,7,10,11-hexaheptyloxytriphenylen e (**3c**) and 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene (**14b**)*

Compounds **3b**, **3c** and **14b** were prepared by methods analogous to the above. Their spectral data were in accordance with literature data [1, 7].

2.2.3. *Nitration of 2,3,6,7,10,11-h exabutyloxytriphenylene: synthesis of compounds **4a**, **5a** and **6a***

Procedure a: Compound **3a** (500 mg, 0.76 mmol) was dissolved in a mixture of diethyl ether (10 ml) and glacial acetic acid (2.5 ml). To this was added 0.2 ml of 98% HNO_3 and the mixture was stirred at room temperature for 15 min; it was worked-up by adding H_2O and extracting with CH_2Cl_2. The crude product was purified by column chromatography to yield 350 mg (66%) of the mononitro derivative **4a** and 50 mg (9%) of the dinitro derivative **5a**. When the amount of HNO_3 was increased to 1.5 ml and the reaction mixture was stirred for 2 h, it yielded 40 mg (8%) of the mononitro, 300 mg (53%) of the dinitro and 60 mg (10%) of the trinitro derivatives. Similarly when the reaction was carried out with 2.5 ml of HNO_3 for 68 h, it furnished 20 mg (4%)



Scheme 3. Synthesis of monohydroxymononitrotriphenylene derivatives.

of mononitro, 40 mg (7%) of dinitro and 150 mg (25%) of trinitro derivatives.

Procedure b: To a solution of compound **3a** (500 mg, 0.76 mmol) in a mixture of CH_2Cl_2 (10 ml) and nitromethane (40 ml), 0.05, 0.1 and 0.15 ml of 98% HNO_3 was added in three different batches and the mixtures were stirred at room temperature for 15 min. After working up by adding H_2O and extraction with CH_2Cl_2, the crude products were purified by column chromatography. Batch one gave 500 mg (94%) of mononitro derivative, batch two gave 50 mg (9%) of mononitro, 400 mg (70%) of dinitro and 25 mg (4%) of trinitro derivatives, while batch three afforded 475 mg (79%) of trinitro-H4TP. Spectral data for **4a**, **5a** and **6a** have been given in ref. [18].

2.2.4. *Nitration of 2,3,6,7,10,11-hexapentyloxytriphenylene: synthesis of compounds **4b**, **5b** and **6b***

Hexapentyloxytriphenylene was prepared and nitrated as described above by *procedure b* to afford:

4b (90%), MS: M^+ 789.2, ^{1}H NMR: δ 7.83, s, 1H; 7.70, 2s, 3H; 7.41, s, 1H, 4.16, m, 10H; 4.03, t, 2H; 1.82 m, 12H; 1.51 m, 24H; 0.89, m, 18H.

5b (65%), MS: M^+ 834.3; ^{1}H NMR: δ 7.81, s, 1H; 7.69, s, 1H; 7.57, s, 1H; 7.43, s, 1H; 4.25, m, 8H; 4.03, t, 4H; 1.8–1.4, m, 36H; 0.98, m, 18H.

6b (68%), MS: M^+ 879.2; ^{1}H NMR: δ 7.54, s, 3H; 4.23, t, 6H; 4.08, t, 6H; 1.9, m, 6H; 1.8, m, 6H; 1.45, m, 24H; 0.93, m, 18H.

2.2.5. *Nitration of 2,3,6,7,10,11-hexaheptyloxytriphenylene: synthesis of compounds **4c**, **5c** and **6c***

Hexaheptyloxytriphenylene was prepared and nitrated as described above by *procedure b* to afford:

4c (88%), MS: M^+ 957.2, ^{1}H NMR: δ 7.80, s, 1H; 7.69, s, 1H; 7.66, s, 2H; 7.39, s, 1H, 4.11, m, 10H; 3.97, t, 2H; 1.8 m, 12H; 1.5 m, 48H; 0.83, m, 18H.

5c (45%), MS: M^+ 834.3; ^{1}H NMR: δ 7.84, s, 1H; 7.72, s, 1H; 7.58, s, 1H; 7.44, s, 1H; 4.25, m, 8H; 4.03, t, 4H; 1.9–1.2, m, 60H; 0.98, m, 18H.

6c (70%), MS: M^+ 879.2; ^{1}H NMR: δ 7.54, s, 3H; 4.27, t, 6H; 4.08, t, 6H; 1.9, m, 6H; 1.8, m, 6H; 1.45, m, 48H; 0.90, m, 18H.

2.2.6. *1-Amino-2,3,6,7,10,11-hexabutyloxytriphenylene (**7a**)*

Procedure a: 1-Nitro-2,3,6,7,10,11-hexabutyloxytriphenylene **4a** (100 mg, 0.14 mmol) was mixed with 10 mg of 10% Pd on charcoal and 1 ml hydrazine in 10 ml ethyl acetate and the reaction mixture was heated under reflux for 12 h. The solution was washed with water and the crude product purified by column chromatography to yield 58 mg (60%) of **7a**.

Procedure b: Compound **4a** (100 mg, 0.14 mmol) and $NiCl_2.6H_2O$ (67 mg, 0.28 mmol) were dissolved in THF–MeOH (2:1, 20 ml); $NaBH_4$ (21 mg, 0.56 mmol) was added in portions at room temperature, and the mixture was stirred for 30 min. The resulting black precipitate was filtered and washed with ethyl acetate.

The filtrate was extracted with ethyl acetate and the crude product was purified by column chromatography to yield 70 mg (73%) of **7a** [18].

2.2.7. *1-Acetylamino-2,3,6,7,10,11-hexabutyloxytriphenylene (**8a**)*

1-Amino-2,3,6,7,10,11-hexabutyloxytriphenylene **7a** (20 mg, 0.03 mmol) was stirred with acetic anhydride and pyridine (0.5 ml each) at room temperature for 12 h; water was added and the solution extracted with ethyl acetate. The crude product was purified by column chromatography to yield 15 mg (71%) of **8a** [18].

2.2.8. *α,α′-Diazo-2,3,6,7,10,11-hexabutyloxytriphenylene (**9a**)*

1-Amino-2,3,6,7,10,11-hexabutyloxytriphenylene **7a** (100 mg, 0.15 mmol) was stirred in acetic acid (5 ml) and CH_2Cl_2 (10 ml) at 0°C. A solution of sodium nitrite (48 mg, 0.7 mmol) in 1 ml of water was added drop-wise and the mixture was stirred at room temperature for 30 min and at 40°C for 1 h. Water was added and the product and extracted with dichloromethane; after removing the solvent it was purified by column chromatography to yield 60 mg (59%) of **9a** [18].

2.2.9. *1,5-Diamino-2,3,6,7,10,11-hexabutyloxytriphenylene (**10a**)*

Dinitrotriphenylene **5a** (500 mg, 0.67 mmol) and $NiCl_2.6H_2O$ (950 mg, 4 mmol) were dissolved in THF–MeOH (1:1, 20 ml). $NaBH_4$ (300 mg, 8 mmol) was added in portions at room temperature to the resulting solution, which was stirred for 30 min and filtered. The black precipitate was washed with ethyl acetate. The filtrate was extracted with ethyl acetate and the crude product purified by column chromatography over silica gel; it was then eluted with hexane–dichloromethane mixture to yield 275 mg (60%) of diamino-hexabutyloxytriphenylene **10a**. MS: $M^{+\cdot}$ 690.3; ^{1}H NMR: δ 8.55, s, 1H; 8.24, s, 1H; 7.68, s, 1H; 7.19, s, 1H; 4.55 (very broad NH protons signal); 4.09, m, 12H; 1.8, m, 12H; 1.5, m, 12H; 0.95, m, 18H.

2.2.10. *1,5,10-Triamino-2,3,6,7,10,11-hexabutyloxytriphenylene (**11a**)*

Trinitrotriphenylene **6a** (500 mg, 0.63 mmol) and $NiCl_2.6H_2O$ (1.8 g, 7.6 mmol) were dissolved in THF–MeOH (2:1, 20 ml). $NaBH_4$ (580 mg, 15 mmol) was added in portions at room temperature, and the mixture was stirred for 30 min and filtered. The black precipitate was washed with ethylacetate. The filtrate was extracted with ethyl acetate and the crude product purified by column chromatography over silica gel; the product was eluted with dichloromethane to yield 275 mg of triaminohexabutyloxytriphenylene **11a**. MS: $M^{+\cdot}$ 705.3; ^{1}H NMR: δ 8.08, s, 3H; 4.57, s, 6H; 4.11, t, 12H; 1.87, m, 12H; 1.57, m, 12H; 1.0, m, 18H.

2.2.11. *1,5-Diacetylamino-2,3,6,7,10,11-hexabutyloxytriphenylene (**12a**)*

The diaminohexabutyloxytriphenylene **10a** (500 mg, 0.72 mmol) was stirred with acetic anhydride and pyridine (1 ml each) at room temperature for 12 h. Water was added and the resultant solution extracted with ethyl acetate; the crude product was purified by column chromatography over silica gel and elution with dichloromethane–ethyl acetate to yield 390 mg (70%) of diacetylaminohexabutyloxytriphenylene **12a**. MS: $M^{+\cdot}$ 774.2; ^{1}H NMR: due to the poor solubility of the material in common solvents a good NMR spectrum could not be obtained.

2.2.12. *1,5,10-Triacetylamino-2,3,6,7,10,11-hexabutyloxytriphenylene (**13a**)*

Triaminohexabutyloxytriphenylene **11a** (500 mg, 0.71 mmol) was acetylated as above to yield 400 mg (68%) of **13a**. MS: $M^{+\cdot}$ 831.3; ^{1}H NMR: due to the poor solubility of the material in common solvents a good NMR spectrum could not be obtained.

2.2.13. *Nitration of 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene*

To a solution of compound **14a** (500 mg, 0.83 mmol) in diethyl ether (30 ml) and glacial acetic acid (12 ml), was added 0.5 ml of 98% HNO_3 and the mixture was stirred at room temperature for 1 h. It was worked-up by adding H_2O and extracting with ether. The crude product was purified by column chromatography to yield 300 mg (56%) of **15a** [18]. In subsequent experiments yields in the range 20–55% were observed.

2.2.14. *Nitration of 2-hydroxy-3,6,7,10,11-pentapentyloxytriphenylene*

Compound **14b** was nitrated as above to yield **15b** (25%). ^{1}H NMR: δ 7.87, s, 1H; 7.79, s, 2H; 7.75, s, 1H; 7.41, s, 1H; 6.54, s, 1H; 4.23, m, 8H; 4.08, t, 2H; 1.90, m, 10H; 1.51, m, 20H; 0.97, m, 15H.

2.2.15. *Acetylation of compounds **15a** and **15b***

Compounds **15a** and **15b** were acetylated with acetic anhydride and pyridine by the usual method. Purification of the crude product furnished the acetylated compounds **16a** and **16b**.

16a: MS: $M^{+\cdot}$ 691.3; ^{1}H NMR: δ 7.9, s, 1H; 7.72, s, 1H; 7.70, s, 1H; 7.61, s, 1H; 7.32, s, 1H; 4.18, m, 8H; 3.99, t, 2H; 2.3, s, 3H; 1.9, m, 10H; 1.56, m, 10H; 0.95, m, 15H.

16b: ^{1}H NMR: δ 7.97, s, 1H; 7.79, s, 2H; 7.77, s, 1H; 7.38, s, 1H; 4.23, m, 8H; 4.05, t, 2H; 2.37, s, 3H; 1.9, m, 10H; 1.48, m, 20H; 0.97, m, 15H.

2.2.16. *Synthesis of compounds* ***17a*** *and* ***17b***

A mixture of compound **15a** (50 mg, 0.08 mmol), K_2CO_3 (22 mg, 0.16 mmol) and 2-bromoethanol (17 mg, 0.16 mmol) in butanone-2 (10 ml) was heated under reflux for 12 h. The reaction mixture was worked-up by adding H_2O and extracting with ether. The crude product was purified by column chromatography over silica gel and the product was eluted with hexane–dichloromethane to yield 50 mg (93%) of alkylated product **17a**. MS: $M^{+\cdot}$ 693.2; ^{1}H NMR: δ 7.92, s, 1H; 7.79, s, 1H; 7.76, s, 1H; 7.75, s, 1H; 7.46, s, 1H; 4.39, t, 2H; 4.24, m, 8H; 4.08, t, 2H; 3.92, m, 2H; 2.55, t, 1H; 1.89, m, 10H; 1.58, m, 10H; 1.05, m, 15H.

Compound **17b** was prepared as described above in 88% yield. ^{1}H NMR: δ 7.93, s, 1H; 7.80, s, 1H; 7.77, s, 2H; 7.45, s, 1H; 4.39, t, 2H; 4.24, m, 8H; 4.08, t, 2H; 3.92, m, 2H; 2.58, t, 1H; 1.89, m, 10H; 1.58, m, 20H; 1.05, m, 15H.

3. Results and discussion

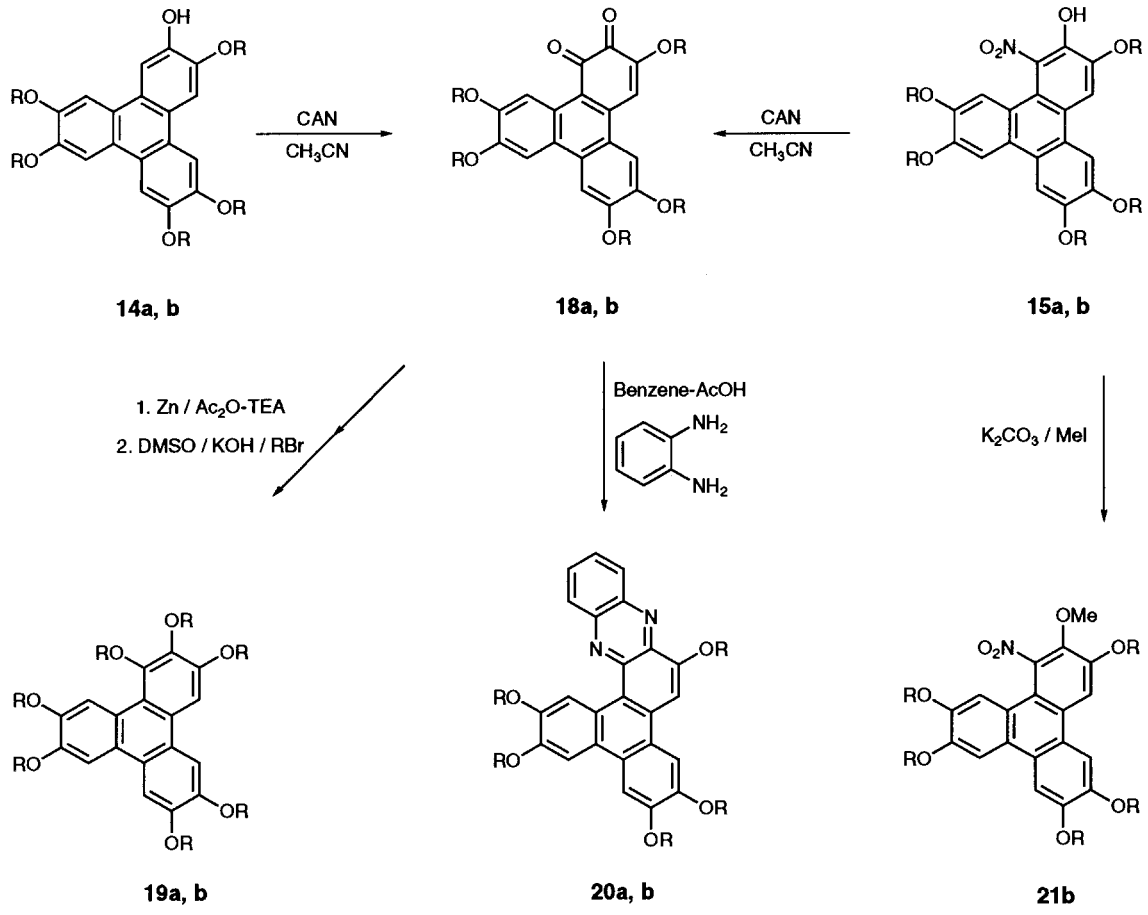
In hexaalkoxytriphenylenes, only the 1, 4, 5, 8, 9 and 12 positions ('bay regions') are free for further substitution. Halogenation [19, 20] and nitration [15, 20] of these derivatives have recently been reported. Chlorination of 2,3,6,7,10,11-hexahexyloxytriphenylene (H6TP) with iodine monochloride gives a mixture of 1-chloro-, 1,8-dichloro and 1,5-dichloro-H6TP. Under exhaustive conditions it furnishes 1,4,5,9-tetrachloro-H6TP [19]. Praefcke *et al.* have also reported the synthesis of 1-chloro-H6TP and 1-bromo-H6TP by the chlorination of H6TP with aluminium trichloride/sulphuryl chloride and bromination of H6TP with bromine in carbon tetrachloride. Nitration of hexahexyloxytriphenylene has been reported to give exclusively the α-nitro product [15, 20].

When we nitrated different hexaalkoxytriphenylenes, the major mononitro product was always contaminated with a minor product that could be isolated by repeated column chromatography. From the spectral analysis it was identified as the dinitro derivative of the hexaalkoxytriphenylenes. When the concentration of HNO_3 and time of the reaction was increased, formation of the trinitro derivative occurred in addition to the dinitro derivative as the major product. About 60% of the dinitro and 10% of the trinitro compound could easily be isolated from this mixture. Efforts to push the reaction towards the trinitro derivative by using excess HNO_3 and longer time yielded only a maximum 25% of the trinitrated product. However, this situation changed dramatically when we changed the solvent system from ether–acetic acid to dichloromethane–nitromethane and the trinitration was complete within 15 min at room temperature with very high yield. This trinitration proceeded with high regioselectivity to give exclusively one isomer having *C*3 symmetry as evident from its ^{1}H NMR, showing only one sharp singlet for three equivalent aromatic protons. The use of about 1 equivalent of HNO_3 gives almost quantitatively the mononitrotriphenylenes in this solvent system and the formation of the dinitro compound can be regulated by the amount of nitric acid.

While the synthesis of mono- and trinitro-triphenylene can be achieved without any side product, we could not prepare the dinitro derivative selectively and the product was always a mixture of the three derivatives. However, they can be separated easily by simple column chromatography. As only the symmetrical 1,5,9-trinitro-2,3,6,7,10,11-hexaalkoxytriphenylene is formed and the dinitro derivative may be considered as the precursor of this trinitro derivative, the structure of the dinitro product is assigned as 1,5-dinitro-2,3,6,7,10,11-hexaalkoxytriphenylene. The ^{1}H NMR data also support this structure, however, the possibility of the second nitro group at some other position cannot be ruled out completely. Nitration of unsubstituted triphenylene under sulphonylation reaction conditions with sulphuric acid/trifluoroacetic anhydride in nitromethane has been reported to give mononitrotriphenylene in low yield [21]. However, treatment of H4TP with sulphuric acid/trifluoroacetic anhydride in nitromethane under our reaction conditions does not give any nitrated product, indicating that nitromethane is not acting as nitrating agent, but a better solubility of the reactants in this solvent system could be the reason for such facile synthesis.

Mononitration of the monohydroxypentaalkoxytriphenylenes **14a** and **14b** (scheme 3) gives monohydroxymononitropentaalkoxytriphenylenes **15a** and **15b**. Oxidation of these monohydroxymononitro derivatives with ceric ammonium nitrate (CAN) gives ring-oxidized products 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones **18a** and **18b** (scheme 4).

The same diquinones were also obtained when 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylenes **14a** and **14b** were oxidized with CAN. We utilized these *ortho*-quinones to prepare a novel series of heptaalkoxytriphenylene discotic LCs [22]. 1,2-phenylenediamine condenses very readily with these diquinones to yield novel phenanthrophenazine derivatives (scheme 4) which were characterized from their UV, mass spectrometry, ^{1}H and ^{13}C NMR data [23]. The greater activating strength of the –OH group, less steric hindrance and the above chemical transformations suggest the nitration takes place *ortho*- to the phenolic group, i.e. at the C-1



Scheme 4. Synthetic routes to pentaalkoxytriphenylene-1,2-diones and their derivatives.

position. This is also supported from the fact that no *n*Oe effect was observed between any aromatic proton and methoxy group in compound **21b** (scheme 4) which was prepared by the methylation of monohydroxymononitropentapentyloxytriphenylene **15b**. We are also trying to grow single crystals of various derivatives derived from monohydroxymononitrotriphenylenes **15a** and **15b** for X-ray analysis. Details of this work will be published in due course.

Acetylation of **15a** and **15b** with acetic anhydride and pyridine gives the acetates **16a** and **16b** (scheme 3). Alkylation of **15a** and **15b** with bromoethanol furnishes compounds **17a** and **17b**. The mononitromonohydroxy derivatives such as **15** and **17** are extremely valuable intermediates, as functionalities such as the hydroxy group can be further derivatized, for example, to acrylates, vinyl ethers, etc., having potential for the preparation of functionalized liquid crystal polymers.

Alkoxynitrotriphenylenes are valuable precursors to several other derivatives, including amino, mono- and di-alkylamino, acylamino, azo, etc. Nitrotriphenylenes **4a**, **5a** and **6a** were easily reduced to the corresponding amino derivatives **7a**, **10a** and **11a** with hydrazine and palladium or with nickel chloride and sodium borohydride (scheme 2). Reduction of mononitrotriphenylene **4a** also works well with tin and acetic acid [15] but this method gives very poor results with di- and tri-nitro derivatives. The amino derivative **7a** was readily converted to α,α′-diazo compound **9a** by diazotization of the amine with nitrous acid followed by cyclization. Acylation of amines **7a**, **10a** and **11a** with acetic anhydride in pyridine converted them in to their *N*-acyl derivatives **8a**, **12a** and **13a**. All the products were purified by column chromatography over silica gel followed by recrystallization or precipitation with ethanol. The purity of all the compounds was determined by TLC in three different solvent systems and they were characterized by spectral analysis.

4. Thermal behaviour

The thermal behaviour of all the compounds was investigated by polarizing microscopy and by differential scanning calorimetry. In the case of liquid crystalline materials, classical textures of columnar mesophases appeared upon cooling from the isotropic liquid. These

textures are very similar to known textures for Col_h phases. However, it now appears that significant differences in the supramolecular structure of these mesophases may not be readily discernible from texture alone [4*e*]. Phase transition temperatures and enthalpy measurements were also carried out on 1–2 mg samples using a Perkin-Elmer DSC7 with heating and cooling rates of 10°C min^{-1}. Data from heating and cooling cycles are collected in table 1. The peak temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1}.

As may be seen from the data, compounds **4a**, **4b**, **4c**, **5b**, **5c**, **8a**, **9a**, **16a**, **16b**, **17a** and **17b** were found to be mesogenic. All the mononitro derivatives **4a**, **4b** and **4c**, when cooled from the isotropic liquid come to the ordered columnar (Col_h) phase. While in **4b** and **4c** this phase stays till room temperature without showing any sign of crystallization or other transition, compound **4a** shows another weak transition at 47.7°C. Although no texture change was observed below and above this transition, the fluidity of this low temperature phase was much less than the high temperature mesophase, but this 'plastic' type phase is deformable under strong physical stress. X-ray results (§5 of this paper) confirm that the mesophase formed by **4b** and the high temperature phase of **4a** are hexagonal columnar phases (Col_h) and the low temperature phase of **4a** is more ordered than the Col_h phase. It should be noted that the mesophase of hexabutyloxytriphenylene was recently reported to be more ordered than the Col_h phase and referred to as a plastic discotic (Col_p) phase [4*e*]. Dinitrohexabutyloxytriphenylene **5a** is a crystalline compound and melts at about 109°C, but its higher homologues **5b** and **5c** are room temperature liquid crystals. Trinitrohexabutyloxytriphenylene was found to be a non-mesogenic crystalline material but trinitrohexapentyloxy- and trinitrohexaheptyloxy-triphenylene are only oily liquids at room temperature.

These results are very interesting as the intermolecular interaction between discotic mesogens may be approximated as the sum of two terms: core–core attraction (e.g. dispersion forces in the case of aromatic cores) and interaction amongst the aliphatic side chains. The presence of flexible aliphatic chains is thought to be essential for introducing the conformational freedom which prevents the formation of long range three-dimensional order. Increasing the core–core interactions while keeping some minimal constraints on the side chains, would encourage molecular stacking and lead to the formation of a liquid crystalline mesophase. The introduction of nitro groups into the triphenylene core again has two effects: the polar nature of nitro groups will increase the attraction between the cores, or the steric bulk of the nitro groups, particularly at the bay-region, will increase the core–core separation and the resulting increase in the entropy of side chains may stabilize the mesophase. On the other hand, too much steric hindrance in a poly-nitrated material may completely destroy the mesophase. In the

Table 1. Phase transition temperatures and enthalpies of nitrotriphenylenes. Cr = crystal, Col_h = hexagonal columnar liquid crystalline phase, Col_x = unidentified mesophase, I = isotropic.

Compound	Thermal transitions/°C and enthalpy changes/kJ mol^{-1} in parentheses	
	Heating scan	Cooling scan
4a	Cr 61.2 (9.4) Col_h 141.3 (7.9) I	I 139.3 (8.5) Col_h 47.7 (0.7) Col_x
4b	Col_h 141.4 (7.7) I	I 140.3 (7.7) Col_h
4c	Col_h 129.8 (6.3) I	I 126.6 (5.5) Col_h
5a	Cr 109.1 (19.6) I	I 99.3 (14.8) Cr
5b	Cr 60.6 (15.1) Col_h 96.0 (3.9) I	I 94.0 (3.8) Col_h
5c	Col_h 80–85 (broad peak) I	I 74.0 (1.9) Col_h
6a	Cr 142.1 (23.9) I	I 135.4 (23.3) Cr
7a	Cr 102.2 (24.0) I	I 95.2 (23.7) Cr
8a	Cr 132.9 (31.7) Cr 172.0 (37.8) I	I 163.0 (10.5) Col_h 147.3 (19.9) Cr
9a	Cr 193.0 (1.4) Cr 280.0 (26.3) I	I 257.3 (10.4) Col_h 151.5 (0.3) Col_x
10a	Cr 86.9 (24.6) I	I 76.4 (21.3) Cr
11a	Cr 67.8 (15.9) I	I 45.8 (8.1) Cr
12a	Cr 234.7 (38.6) Cr 240.4 (6.3) I	I 223.9 (44.4) Cr
13a	Cr 278.3 (81.2) I	I 260.7 (63.7) Cr
15a	Cr 106 (dec.)	
15b	Cr 105 (dec.)	
16a	Cr 155.0 (38.6) I	I 145.4 (9.5) Col_h–Cr
16b	Cr 72.8 (0.8) Cr 129.8 (15.8) Col_h 139.2 (10.8) I	I 136.8 (10.3) Col_h
17a	Col_x 127.8 (1.0) Col_h 144.4 (6.6) I	I 140.7 (6.9) Col_h
17b	Cr 95.6 (19.4) Col_h 130.3 (7.0) I	I 127.9 (7.1) Col_h 65.7 (8.3) Cr

case of mononitro derivatives **4a**, **4b** and **4c** the mesophase stability is enhanced significantly. Dinitro-H4TP **5a** is a crystalline material while its higher homologues **5b** and **5c** have a broad mesophase range. All the trinitro derivatives were found to be non-mesogenic indicating that a minor change in molecular structure may have a large effect on the thermal behaviour. A critical balance of core–core attraction, steric hindrance, constraints and free volume of side chains in a molecule is important in making it mesomorphic.

Compound **8a**, when cooled from isotropic liquid, comes to a monotropic columnar phase at 163°C. Its texture resembles that of the Col_h phase but a cover slip shear test indicated it to be more ordered than a Col_h phase. It crystallizes at 147.3°C and these crystals melt at 170°C on heating.

Compound **9a** also shows the Col_h phase on cooling from the isotropic liquid and supercools to room temperature. The texture observed below 151°C or above does not show any significant change, but DSC reveals a weak transition at this temperature. This low temperature phase may be a more ordered plastic type phase as it is quite difficult to deform it by physical stress.

Compound **16a**, on cooling from the isotropic phase, comes to a metastable Col_h phase at about 145°C. This monotropic mesophase has a high crystallization tendency and starts to crystallize in the mesophase. On the other hand, its higher homologue **16b** melts at 129.8°C and clears at 139.2°C. On cooling it shows the Col_h phase at 136.8°C and supercools to room temperature; it then crystallizes upon keeping for a few minutes at room temperature. The first heating of this compound also shows a crystal-to-crystal transition at 72.8°C.

Compound **17a** upon cooling from isotropic liquid shows the classical texture of a Col_h phase at 140.7°C and can be easily sheared by a small physical force. It supercools to room temperature. On heating it shows a broad weak transition at 127.8°C and finally clears at around 145°C. This thermal behaviour was found to be reversible on subsequent heating and cooling cycles. Similarly, its higher homologue **17b** shows melting and clearing transitions at 95.6°C and 130.3°C respectively. On cooling the Col_h phase appears at 127.9°C and it crystallizes at 65.7°C.

5. X-ray diffraction studies

We have studied two representative molecules among those which exhibit mesophases. The Guinier 1d diffractometer (Huber-Guinier System 600) was used for accurate measurement of the peak positions in the low and wide angle regions. The line-beam from the Cu target X-ray tube is focused with the doubly bent quartz crystal monochromator to give the Cu-$K_{\alpha 1}$ radiation which illuminates the sample. The counter tube is used as the detector. The diffractometer was calibrated with the (1 1 1) reflection from a Si powder standard; Lindemann glass capillaries (1.0 mm diameter) were used as sample containers.

5.1. *Mononitrohexapentyloxytriphenylen e (**4b**)*

The X-ray diffraction scans (1d) were recorded in the Guinier diffractometer with the sample temperature at 50 ± 1°C, figure 1. They showed two diffuse peaks in the wide angle region; one of them was broad and weak. The broad diffuse peak (A1) corresponds to a *d*-spacing of 4.35 Å which is quite close to the usually observed mean distance (4.5 Å) between the alkyl chain molecules in *n*-alkane liquids [24]. The broad nature of the diffuse peak shows that the alkyl chains are in the liquid-like state. The other comparatively narrower and strong diffuse peak (B1) gives an average distance of 3.62 Å which suggests that this arises from the molecular cores loosely stacking one on top of the other along the column. The diffuse nature of the peak implies that there is only short range order among the molecular cores along the column. Similar diffuse peaks have been observed in the X-ray study of alkoxytriphenylenes [25]. In the low angle region, one strong and two weak, fairly sharp peaks were observed (see table 2). The ratio of the reciprocal of the *d*-spacings of the weak peaks to that of the strong lowest Bragg-angle peak is 1.0 : 1.747 : 2.018. This ratio is consistent with that expected if the lattice is two dimensional hexagonal with the first peak assigned the index (1 0). These features are very similar to that observed for the hexagonal columnar mesophases formed by alkoxy- and thio-triphenylenes [4*e*, 15, 26]. Thus, the mononitro-hexapentyloxytriphenylene (mononitro-H5TP) forms a hexagonal columnar phase in which the columns formed by the stacking of molecular cores one on top

Table 2. X-ray diffraction data for mononitro-H5TP (4b) and mononitro-H4TP (4a) in the mesophase.

		Peak-positions/Å					
		Low angle region				Wide angle region (diffuse peaks)	
Compound name	Temperature/°C	(1 0)	(1 1)	(2 0)	(2 1)	Core-core peak	Alkyl chain peak
Mononitro-H5TP (**4b**)	50 ± 1	17.52	10.03	8.68	—	3.62	4.35 ± 0.02
Mononitro-H4TP (**4a**)	58	16.12	9.34	8.06	6.02	3.63	4.26 ± 0.02

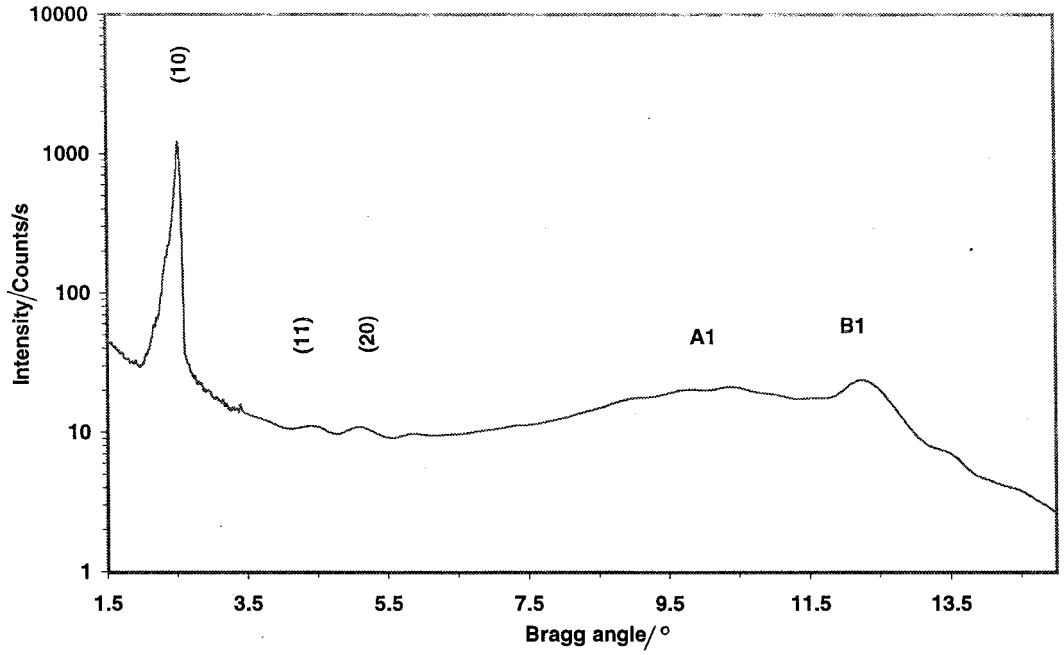


Figure 1. X-ray diffraction scan for the hexagonal columnar phase (Col_h) of mononitro-H5TP.

of the other with only short range order among the cores (20.4 Å, about 5 nearest neighbor distance along the column) are arranged in a two dimensional hexagonal lattice. Following the nomenclature used in the structural studies of alkoxy- and thiotriphenylenes [4*e*, 15, 26] this phase is classified as Col_h.

The mean distance between the molecular cores along the column, 3.62 Å, is smaller than the corresponding distance, 3.7 Å, observed for mononitro-H6TP [15] which is obtained from photographic measurements. The distance between the centres of the nearest neighbour columns is 20.1 ± 0.1 Å (mean of the values obtained from all the observed (*h k*) reflections). The corresponding distance for mononitro-H6TP obtained from the (1 0) peak position reported by Boden *et al.* [15] is 21.9 Å. The decrease in the intercolumnar distance for mononitro-H5TP agrees closely with that calculated from the length of one CH_2 unit, which agrees with what should be expected from the liquid crystalline nature of the system.

5.2. *Mononitrohexabutyloxytriphenylene (**4a**)*

The 1d Guinier diffractometer scans were recorded with the sample temperature held at 58°C, figure 2. Two diffuse peaks were observed in the wide angle region: the weak and broad one occurred at 4.26 Å, the strong and comparatively narrower one at 3.63 Å. These two peaks are very similar in appearance to those observed for mononitro-H5TP, suggesting that the weak and broad peak arises from the liquid-like order of the alkyl chains, and the strong and narrower one from the stacking of the molecular cores one on top of the other along the column with only short range order (23.8 Å, about 6 nearest neighbors along the column) among them. In the low angle region four sharp peaks are observed; one of them is very strong and other three weak. The ratio of the reciprocal of the *d*-spacings of the weak peaks to that of the strong lowest Bragg-angle peak is 1.0 : 1.726 : 2.000 : 2.678. Hence the lattice is two dimensional hexagonal. The intercolumnar distance calculated as the mean of those obtained from all the observed (*h k*) reflections is 18.6 ± 0.1 Å. The decrease in the column diameter for mononitro-H4TP from that of mononitro-H5TP is 1.5 Å. This is comparable to the decrease observed when the mononitro-H5TP intercolumnar distance is compared with that for mononitro-H6TP.

In addition to the high temperature phase which has just been described, mononitro-H4TP has a monotropic transition which is clearly seen in DSC. Preliminary X-ray investigations indicate that the monotropic phase is more ordered (referred to as 'plastic' phase in the discussion of the thermal behaviour and the texture observations) than the hexagonal columnar phase observed at high temperature [27]. Some of the other mono-substituted triphenylene derivatives with C_4-chain length also exhibit a monotropic transition in DSC. Further characterization of the nature of these phases is under progress which will be reported elsewhere.

6. Conclusion

We have reported on the synthesis of various mono-, di- and tri-nitrotriphenylene derivatives. The nitro group

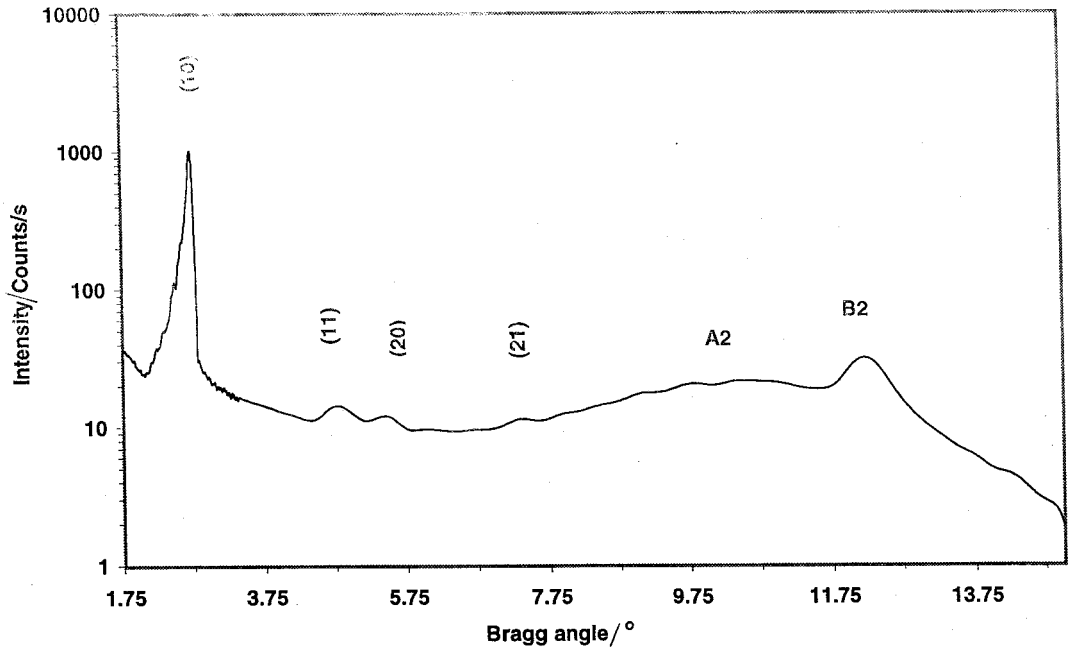


Figure 2. X-ray diffraction scan for the hexagonal columnar phase (Col_h) of mononitro-H4TP.

is a valuable precursor to a variety of substituents in aromatic systems. The aromatic nitro groups can be reduced to the amino groups with a number of reducing agents and the amines can be further alkylated or acetylated with different alkyl halides or acyl halides. Diazotized amines can be cyclized to α,α′-diazo compounds. Thus, mono-, di- and tri-nitrotriphenylenes open the door for several other triphenylene derivatives. The hydroxyl function has the potential to allow further conversion to dimers, oligomers and polymers. Incorporation of both nitro and hydroxy groups in triphenylene discotics will lead to a variety of functionalized triphenylene derivatives that can be used in molecular electronics. The syntheses of various functionalized triphenylene dimers, oligomers and polymers are currently being investigated in our laboratory.

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