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New branched chain tricycloquinazoline derivatives: a room temperature electron deficient discotic system

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Tricycloquinazoline (TCQ) based discotic liquid crystals have recently received increasing attention due to their interesting physical and electronic properties. Three new branched chain TCQ derivatives **6a–c** were prepared and characterized. One of them, **6c,** was found to be mesogenic at room temperature, having a very broad mesophase range. The small angle X-ray scattering of this compound shows a centre to centre distance of 3.29 Å, one of the lowest core–core separations known in discotic liquid crystal systems. This very close packing of the molecules in the column in conjunction with the stability of the mesophase well below and above the ambient temperature makes it very suitable for carrying out physical studies.

Introduction

In the last decade there has been an enormous development in utilizing liquid crystals (LCs) *e.g.* in different display devices.[1] More recently, discotic liquid crystals[2] have been considered as new materials for one-dimensional transport of charge and energy and their potential applications in conducting, photoconducting, optical data storage, light emitting diode, photovoltaic solar cell, *etc.*, devices have been sought.[3] To further explore these intriguing materials, novel ordered systems with different physico-chemical properties are required. We recently initiated a research program focusing on the synthesis and characterization of novel discotic liquid crystals based on various aromatic cores. Here we report on the synthesis, characterization and X-ray studies of some new TCQ derivatives.

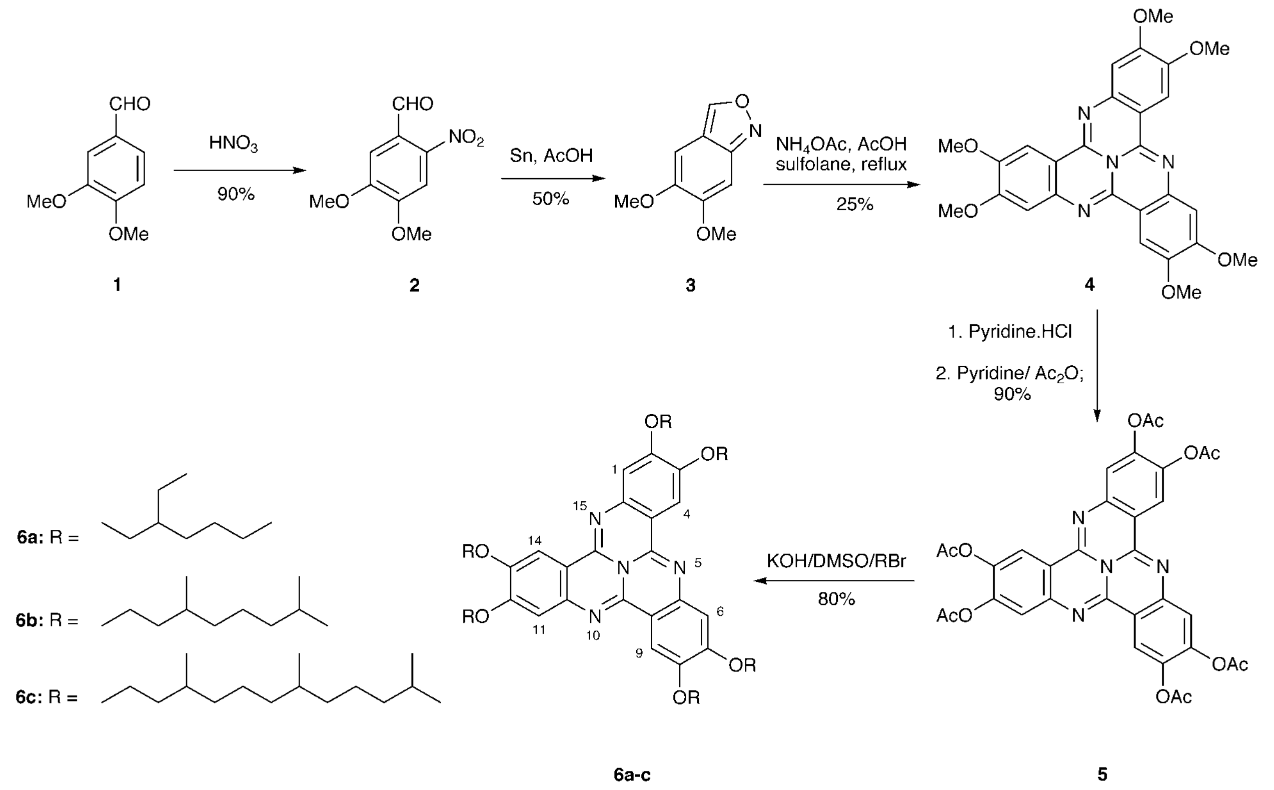
TCQ is a molecule of both biological and physical interest. It is readily formed in pyrolytic reactions of a number of anthranilic acid derivatives, *e.g.* methyl anthranilate.[4,5] The wide occurrence of the latter in plant materials and the ease of TCQ production from them by combustion have boosted an extensive study of the carcinogenic activity of TCQ.[6] The high carcinogenicity of TCQ is probably due to its ability to intercalate into DNA.[6] The heterocyclic TCQ molecule as a core for discotic liquid crystals is attractive for many reasons: it possesses C_3 symmetry, its derivatives are coloured, it shows extraordinary thermal and chemical stability, it sublimes without decomposition under atmospheric pressure at very high temperatures, it tolerates strong oxidants such as chromic anhydride in concentrated sulfuric acid, it is highly resistant to biological oxidation and it does not couple with diazotized arylamines.[4,7] The molecule exhibits intriguing physical characteristics, such as a low ionization potential and interesting spectroscopic and electronic properties.[8,9] Most of the discotic liquid crystals are electron rich systems, and therefore, upon doping with electron acceptors produce p-doped electronically conducting discotic LCs. The π deficient nature of TCQ derivatives make them suitable for doping with electron donors. The first organic one-dimensional n-conducting discotic LC based on TCQ has recently been reported.[10]

We have earlier reported a broad spectrum of homologous 2,3,7,8,12,13-hexakis(thioalkoxy)tricycloquinazoline derivatives and 2,3,7,8,12,13-hexaalkoxytricycloquinazoline derivatives with alkyl side chain lengths varying from 3 to 18 carbon atoms.[8,9] Photo induced charge carrier mobility in the order of 10^{-3} cm^2 V^{-1} s^{-1} in the Col$_h$ phase of the hexathio-TCQ derivative has been observed but because of its very high clearing temperature, full characterization could not be done.[11] We have also studied the self-assembled monolayers of these materials on gold surfaces by scanning tunneling microscopy,[12] infrared spectroscopy, quartz crystal microbalance, and atomic force microscopy.[13] The two major problems in further exploring these interesting materials are the poor yield and high melting and clearing points of all the TCQ discotics reported so far. For various physical studies like photoconductivity, LED, one-dimensional energy migration *etc.*, we were in need of a low clearing, broad mesophase and preferably a room temperature liquid crystalline TCQ derivative. We have recently reported[14] a high yielding process for the preparation of hexaalkoxy-TCQ derivatives and here we wish to report the synthesis and characterization of some new branched chain TCQ derivatives, one of which exhibits a columnar mesophase at room temperature.

Experimental

General information

Chemicals and solvents (AR quality) were obtained locally and used as such without any purification. Column chromatographic separations were performed on silica gel (70–230 and 200–400 mesh). Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). Mass spectra were recorded on a JEOL JMS-600H spectrometer in FAB$^+$ mode using an *m*-nitrobenzyl alcohol (NBA) matrix. ^{1}H NMR spectra were recorded in CDCl$_3$ on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer. All chemical shifts are reported in δ (ppm) units downfield from Me$_4$Si, and J values are given in Hz. UV spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 spectrometer. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer). X-ray studies were performed using an image plate detector (MAC Science DIP1030). Unoriented samples contained in sealed Lindemann glass capillaries were irradiated with Cu Kα rays obtained from a sealed-tube generator (Enraf-Nonius FR 590) in conjunction with double



Scheme 1 Synthesis of branched hexaalkoxytricycloquinazolines.

mirror focusing optics. The synthesis of different TCQ derivatives is outlined in Scheme 1. Compounds **1–5** and branched chain alkyl bromides were prepared as reported.[9,15]

Synthesis of 6a–c

Powdered KOH (135 mg, 2.4 mmol) was mixed with DMSO (2 ml) at room temperature and stirred for 10 min. Hexa-acetoxy-TCQ (66.8 mg, 0.1 mmol) followed by the appropriate branched chain alkyl bromide (2.4 mmol) was added and the reaction mixture was stirred at 55 °C for 24 h and then worked up by addition of ice–water and extraction with diethyl ether. The crude product was purified by column chromatography (silica gel, hexane–ethyl acetate) and crystallized or precipitated with ether–acetone to afford pure yellow materials in about 80% yield.

UV–vis data. All the derivatives give similar spectra having λ_{max} (CHCl$_3$): 282, 322, 400, 422, 450 and 482 nm.

IR data. (CHCl$_3$): All the three compounds have the same spectrum, ν_{max} 3660, 2920, 2855, 1625, 1485, 1465, 1385, 1290, 1100, 1000, 870 cm^{-1}.

MS data. 6a: *m/z* 1089.0 (M+H, 100%); **6b**: *m/z* 1257.8 (M+H, 100%); **6c**: *m/z* 1677.8 (M+H, 100%).

^{1}H NMR data. 6a: δ 7.69 (s, 3H), 6.91 (s, 3H), 4.02 (t, 12H, J=6.2), 1.85 (m, 6H), 1.6–1.3 (m, 48H), 0.96 (m, 36H).

6b: δ 7.72 (s, 3H), 6.92 (s, 3H), 4.17 (m, 12H, J=6.2), 2.0–1.2 (m, 78H), 0.98 (m, 18H) and 0.88 (d, 36H).

6c: δ 7.72 (s, 3H), 6.92 (s, 3H), 4.17 (m, 12H, J=6.2), 2.0–1.15 (m, 102H), 0.99 (m, 18H) and 0.86 (d, 54H).

Results and discussion

In calamitic LCs, broadening of the mesophase range and lowering of clearing temperature are often accomplished by mixing of different components to achieve eutectic mixtures but such mixing is not common in the case of discotic liquid crystals. The use of branched chains to modify the thermal properties of a single component system has been well documented and some effects of the introduction of branched chains into mesogens on the mesomorphism have been summarised by Ohta and co-workers.[16] The hexagonal columnar phase of octakis(dodecyl)tetrapyrazinoporphyrazine changes to the tetragonal columnar phase when the peripheral chains are branched (2-ethylhexyl).[17] Tetrakis(*n*-pentyldithiolato)dinickel(II) has a monotropic discotic lamellar phase but the branched chain-substituted derivative, tetrakis(1-ethylpentyldithiolato)dinickel(II) shows an enantiotropic hexagonal columnar phase in addition to the monotropic discotic lamellar phase.[16] Collard and Lillya recently reported[18] that when the aliphatic side chains of hexa(*n*-alkanoyloxy)benzenes and hexakis(*n*-alkanoyloxy)cyclohexanes are branched, the columnar mesophase is widened but the type of mesophase formed was not affected by the introduction of branching. A similar strategy has been applied by Schouten *et al.* to the phthalocyanine molecule.[15,19] The mesophase in all the branched chain phthalocyanines is broadened significantly and the most dramatic effect was observed in the case of PcO12,3 with the highly branched 3,7,11-trimethyldodecyloxy chain where the clearing temperature is also lowered significantly.[15,19] The decrease in the transition temperature could be due to the disorder caused by branched chains and stereoheterogeneity. The depression of transition temperatures can also be achieved by terminal unsaturation or heteroatom substitution.[18] Crystallization of the liquid crystalline compounds could also be prevented by unsymmetrical chain substitution or polymerization.[20]

We utilized the branched chain substitution strategy to stabilize the mesophase and bring down the clearing temperature of TCQ discotics. The synthesis of new branched chain TCQ derivatives is outlined in Scheme 1. Polymethoxyarenes have been commonly used as precursors for the synthesis of polyether discogens because aromatic methoxy groups may be easily cleaved to give the corresponding phenols, and the latter are conveniently alkylated with alkyl halides. The hexamethoxy-TCQ **4** was assembled following the well known literature method.[9] Demethylation of **4** with pyridine hydrochloride gives the hexaphenol but this polyphenol is not very stable and could be the reason for the poor yields obtained in the final alkylation reaction.[9] We recently observed that protection of phenolic groups by *in-situ* acetylation furnished the hexaacetoxy-TCQ **5** in high yield.[14] The aforesaid hexaacetate can be directly alkylated with various branched chain alkyl bromides to get the desired TCQ derivatives **6a–c** in high yields.

Thermal behaviour

The phase transition temperatures were determined by differential scanning calorimetry (DSC) and optical microscopy (Table 1). Compound **6a** with an ethyl group branched at the β-position of the hexyloxy alkyl chain is found to be non liquid crystalline. It shows a crystal to isotropic transition at 152.8 °C on heating and crystallizes back at 145.7 °C on cooling. The non liquid crystalline nature of this compound could be due to the steric bulk of the ethyl branch close to the aromatic core. In contrast, when the *n*-alkoxy chains are branched with methyl groups as in **6b** and **6c**, both the compounds have a broad range for the $\mathrm{Col_h}$ mesophase. Compound **6b** shows a crystal to $\mathrm{Col_h}$ transition at about 118 °C and it clears at 190.8 °C. Upon cooling, the mesophase texture appears at 186 °C which resembles well those observed for the unbranched TCQ discotics.[8,9] The material crystallises at 99.5 °C. Both the melting and isotropic transitions are reversible in this compound. Substitution of three methyl groups at the 3, 7 and 11 positions of the *n*-dodecyloxy chains results in large changes in the phase transition temperatures. Compound **6c** precipitated out in the liquid crystal form upon the addition of acetone to the ethereal solution of the pure material. Upon heating, it transforms to the isotropic phase at about 143 °C. On cooling this isotropic liquid, the well defined texture of the $\mathrm{Col_h}$ phase appears at 142 °C and it is stable at room temperature. The DSC traces obtained on heating and cooling runs are shown in Fig. 1. As can be seen, the compound **6c** shows a sharp mesophase to isotropic transition at 143.08 °C (peak temperature). The transition reappears on the cooling cycle with very limited supercooling and stays down to −50 °C, the lowest temperature to which the sample was cooled to (see Fig. 1).

X-Ray diffraction studies

Diffraction patterns were recorded at room temperature (RT) and at 127 °C for compound **6c**. Fig. 2a and 2b show the room temperature pattern and the derived one-dimensional intensity *vs.* 2θ profile obtained by integrating over the entire χ (0–360°) range. The overall features observed are consistent with the structure of the $\mathrm{Col_h}$ phase.[21] In the low-angle region, four sharp peaks, one very strong and three weak reflections, are seen whose *d*-spacings are in the ratio of $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$. Identifying the first peak with the Miller index 100, the ratios conform to the expected values from a two-dimensional hexagonal lattice with a disc diameter (or equivalently the inter-columnar distance) of 29 Å. In the wide-angle region two diffuse reflections are seen. The broad one centered on 4.67 Å corresponds to the liquid-like order of the aliphatic chains. The relatively sharper one seen at higher 2θ-values and well separated from the broad one is due to the stacking of the molecular cores one on top of another. It is interesting to note that it can be seen at temperatures not too far from the transition to the isotropic phase. As this is a diffuse peak it suggests that the stacking of the discs within each column is correlated over short distances only. The correlation length calculated using the FWHM of the peak and the Scherrer expression[22] yields values of 63 Å at 127 °C and 109 Å at RT. The average stacking distance (core–core separation) is 3.48 Å at 127 °C and falls in the range observed for a number of materials exhibiting the columnar phase. But remarkably at RT one gets a very low value of 3.29 Å which is only 1% higher than the smallest value reported.[23] It should be noted, however, that the lowest value obtained was in the case of a free-radical sandwich complex with two phthalocyanine cores, which were linked by a lutetium atom. The significance of these numbers should be seen in the light of the following. The columnar organization of these materials provides a one-dimensional pathway for charge transport. The efficiency of the transport depends on the extent of the π–π* overlapping of the neighboring discs within a column. For optimization of the charge transport one would like to maximize the overlapping by decreasing the core–core separation without a loss of the fluid nature of the phase. Hence materials which exhibit a columnar phase but show a small core–core separation are good candidates for rapid intra-columnar charge migration. In fact, the lutetium complex mentioned above shows one of the highest intra-columnar mobilities seen in a columnar liquid crystalline phase.[23] Therefore we believe that the compounds of the present series should be interesting for such investigations.

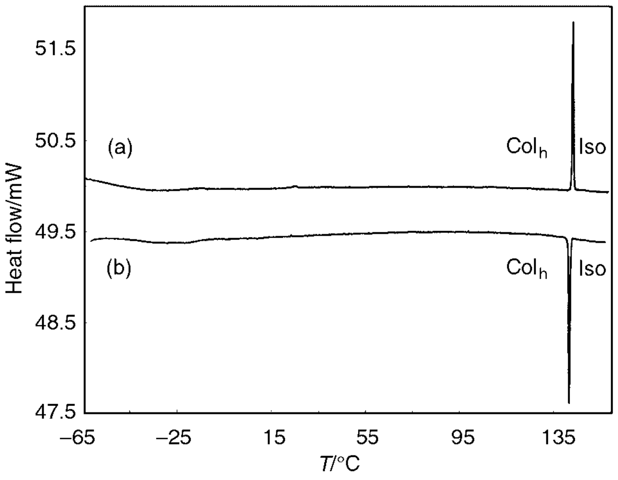


Fig. 1 DSC traces for compound **6c** on (a) heating and (b) cooling (scan rate 5 °C $\mathrm{min^{-1}}$).

Conclusions

Three new TCQ derivatives peripherally substituted with branched alkoxy chains (**6a–c**) were synthesized. Substitution

Table 1 Phase transition temperatures (peak temperatures) and enthalpies of TCQ derivatives **6a–c**. Cr = crystal, $\mathrm{Col_h}$ = hexagonal columnar liquid crystalline phase, Iso = isotropic

Compound	Thermal transitions (°C) and enthalpy changes (kJ $\mathrm{mol^{-1}}$ in parentheses)	
	Heating scan	Cooling scan
6a	Cr 152.8 (40.0) Iso	Iso 145.7 (30.8) Cr
6b	Cr 117.9 (10.1) $\mathrm{Col_h}$ 190.8 (10.5) Iso	Iso 185.9 (9.6) $\mathrm{Col_h}$ 99.5 (7.6) Cr
6c	$\mathrm{Col_h}$ 143.1 (14.1) Iso	Iso 141.6 (13.6) $\mathrm{Col_h}$

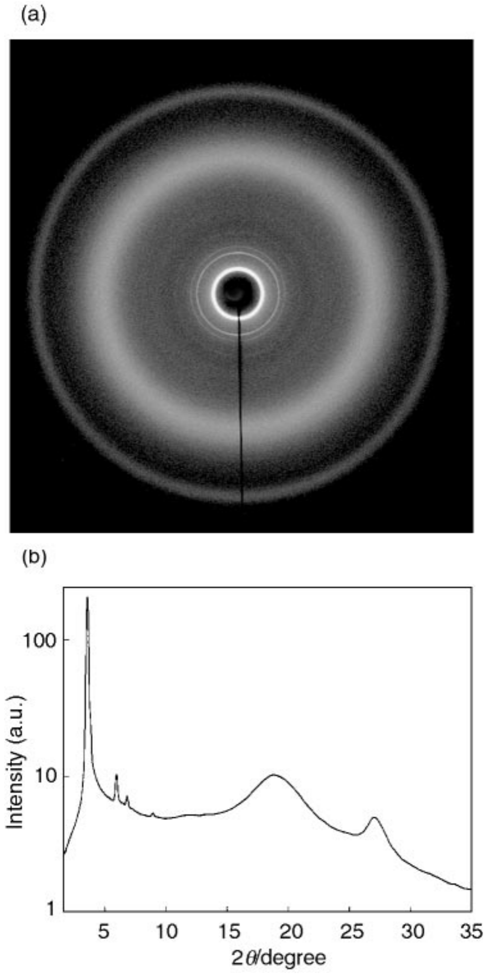


Fig. 2 (a) X-ray diffraction pattern obtained for compound **6c** at room temperature. Notice the two well separated diffuse rings at wide angles; (b) χ-averaged one-dimensional intensity *vs.* 2θ profile derived from (a). The 2θ values for the four sharp peaks at low angles conform to a two-dimensional hexagonal lattice. The first diffuse peak at $2\theta \sim 20°$ is from the aliphatic chains, while the second at higher angles is due to the stacking of the rigid cores within a column giving a core–core separation of 3.29 Å.

of a bulky ethyl group near to the core destroys the mesophase. Two methyl branching in the octyloxy chain at the 3 and 7-positions gives a broad mesophase material having reversible melting and isotropic transitions. Compared to the *n*-alkyl chain TCQ derivatives,[9] in the present case, branching causes depression in the isotropic temperature. Dramatic effects were observed when the peripheral dodecyloxy chains were substituted with three methyl groups at the 3, 7 and 11-positions. A columnar mesophase is observed at room temperature in this compound which does not crystallize until −50 °C. The material also has a significantly low clearing temperature. From X-ray studies, the mesophase formed by the compound is characterized as $\mathrm{Col_h}$ type but with a very short core–core distance. Finally we would like to make the observation that in designing materials for charge migration applications it may be better to have not just broad molecular cores but to introduce branched chains as well. While the former increases the area of overlapping the latter perhaps decrease the melting point and also the core–core separation.

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