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Hexaalkoxytricycloquinazolines: New Discotic Liquid Crystals

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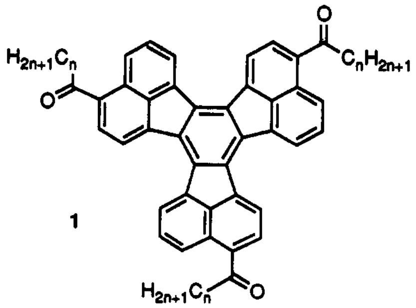
Tricycloquinazoline (TCQ), a molecule of both biological and physical interest, has been found to function as the core fragment for a new family of discotic mesogens, which have C_3 symmetry and six aliphatic side chains. Six representative homologous 2,3,7,8,12,13-hexaalkoxy-TCQ derivatives 5 were synthesized, with alkyl side chain lengths varying from 3 to 16 carbon atoms. These highly fluorescent, heteroaromatic compounds are conveniently obtained by alkylation of hexahydroxy-TCQ, 10. The latter is prepared by trimerization of 5,6-dimethoxyanthranil, 8, followed by demethylation of the resultant hexamethoxy-TCQ, 9. All compounds, 5, are mesogenic within a very broad temperature range. The nature of these new mesophases was studied by DSC and by optical microscopy with polarized light and X-ray diffraction. DSC measurements show highly reversible behavior at both melting and clearing points, indicating high chemical stability. Photomicroscopic pictures show mosaic textures, characteristic of an ordered hexagonal, columnar phase (D_{ho}), that are very similar to those we reported earlier for hexakis(thioalkoxy)-TCQ derivatives 4. The diffraction spacings of two representative compounds (having 5 and 11 carbon atoms in the side chain) in the mesophase are consistent with a two-dimensional hexagonal lattice having unit cell sides of a = 21.2 and 28.7 Å, respectively, and containing one molecule per unit cell.

Introduction

The common discotic mesogen molecules are known to have a flat structure, comprising a rigid core, e.g., polycyclic aromatic structure, and a ring of four to nine aliphatic side chains.[1] The interplay between two main factors determine the tendency of such disk-like molecules to form stable liquid crystalline phases. On the one hand, attractive intermolecular interactions drive toward crystalline order. These interactions include mainly core–core attraction (e.g., dispersion forces in the case of aromatic cores) and hydrophobic interactions between the aliphatic side chains. On the other hand, the presence of flexible aliphatic side chains introduces the conformational freedom which disrupts long range, three-dimensional order. One may expect that increasing core–core attraction (e.g., in mesogens having large, polycyclic aromatic cores) while maintaining some minimal constraints on the number, size, and nature of the side chains would encourage molecular stacking and lead to the formation of a liquid crystalline mesophase.

To pursue this idea, we have focused on the synthesis and characterization of potential discogens that possess big, strongly interacting cores. An interesting example is the family of 1,7,13-trialkanoyldecacyclene derivatives 1, which possess only three side chains and still form columnar liquid crystals over a broad temperature range.[2]



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Another new family of discogens has been recently designed, with the heteroaromatic system of tricycloquinazoline (TCQ) being the core fragment. A broad spectrum of homologous 2,3,7,8,12,13-hexakis(thioalkoxy)-tricycloquinazoline derivatives 4, with alkyl side chain lengths varying from 3 to 18 carbon atoms, were prepared and characterized.[3] All of these highly fluorescent, thermally stable, heteroaromatic compounds which have C_3 symmetry were found to be mesogenic within a very broad temperature range. Their diffraction spacings in the mesophase were consistent with a two-dimensional hexagonal lattice. All of these hexakis(thioalkoxy)-TCQ derivatives 4 were conveniently synthesized by thiolate anion substitution of hexachloro-TCQ, 3, with the latter being prepared by trimerization of 5,6-dichloroanthranil, 2 (Scheme I).[2]

Our attention was focused on TCQ as a potential core for discotic liquid crystals, mainly because of its 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,[4] and it does not couple with diazotized arylamines.[5] TCQ is readily formed in pyrolytic reactions of a number of anthranilic acid derivatives, e.g., methyl anthranilate.[2,6] In fact, the wide occurrence of the latter in plant materials and the ease of TCQ production from it by combustion has boosted an extensive study of the carcinogenic activity of TCQ.[7] The high carcinogenicity of TCQ, probably due to its propensity

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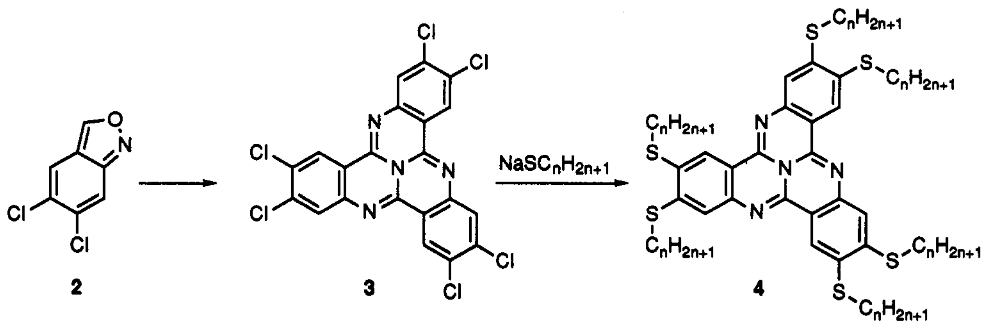
Scheme I



to intercalate into DNA,[7f] points to a strong tendency to stacking and aggregation, as may also be suggested by its high melting point (323 °C)[3,8] and its crystal structure.[9] In addition, TCQ possesses interesting conformational directionality, which arises from its C_3 symmetry.[10] Finally, this system exhibits intriguing physical characteristics, such as a low ionization potential,[11] and interesting spectroscopic properties.[12] All these characteristics make TCQ an especially attractive core of discotic mesogens. In fact, except for the phthalocyanine liquid crystals,[13] very few discotic mesogens having a heteroaromatic core are known.

The unique physicochemical characteristics of our thioether series, **4**,[2] and in particular, their interesting electrochemical properties,[14] as well as their photoconductivity,[15] made the oxygen analogs, hexaalkoxy-TCQ derivatives **5**, an obvious target for our further studies. Unfortunately, all attempts to synthesize these ethers via nucleophilic substitution of **3** using various metal alkoxides afforded the desired hexaalkoxy-TCQ derivatives in very poor yields along with complex mixtures of partially substituted products. Here, we report on an alternative synthetic approach to **5**, as well as on the physical properties of this new family of discotic mesogens.

Results and Discussion

Polymethoxyarenes have been commonly used as precursors for the synthesis of polyether and polyester discogens because aromatic methoxy groups may be easily cleaved to give the corresponding phenols, and the latter are conveniently alkylated or acylated. For example, hexamethoxytriphenylene and hexamethoxytruxene have been employed as precursors in the synthesis of various triphenylene and truxene mesogens.[1] Therefore, we based our alternative synthetic strategy on the preparation of 2,3,7,8,12,13-hexamethoxytricycloquinazoline, **9**, as the key intermediate in the preparation of **5** (Scheme II). Veratraldehyde, **6**, was converted to 2-nitroveratraldehyde, **7**, in 90% yield by nitration at low temperature. Partial reduction of **7** to produce 5,6-dimethoxyanthranil, **8**, was achieved in 54% yield using tin foil and acetic acid.[16] Although much less reactive than electron-deficient anthranils,[17] **7** was successfully trimerized in the presence of ammonium acetate and refluxing sulfolane to produce hexamethoxy-TCQ, **9**, in 27% yield. Demethylation of all six methoxy groups of the latter was carried out in molten pyridinium hydrochloride at elevated temperatures, affording hexahydroxy-TCQ, **10**, in 50% yield. Hexaalkylation of **10** was achieved in low to moderate yields using excess of the appropriate *n*-bromoalkane in KOH/DMSO. All products, **5a–g**, were obtained in the form of yellow-orange solids. They were easily purified by column chromatography on silica gel, followed by recrystallization from hexane. They were characterized by NMR, IR, UV-vis, and fluorescence spectroscopies, as well as by MS and elemental analysis.

Several spectral properties of these new compounds are noteworthy. First, as has already been observed with the thioethers **4**,[2] they exhibit a very strong tendency to aggregate, even at high dilution. This is clearly concluded from the high dependence of their ^{1}H NMR chemical shifts on concentration and temperature. Significant upfield shifts (more than 0.2 ppm) of the aromatic signals are observed when the concentration is increased from 2×10^{-5} M to 2×10^{-2} M, as expected for protons of one molecule that experience the shielding effect of a neighboring one. Second, all members of this family show a very intense molecular ion signal in their mass spectrum (using either chemical ionization or electron impact techniques), and in some cases it is the most abundant ion (where the base peak is usually a very small fragment). We assume that this observation points to a relatively high electron density at the center of the TCQ molecule, leading to the formation of a relatively stable cation radical, localized on the nitrogen atoms.[2] A particularly interesting phenomenon is observed in the negative desorption chemical ionization (DCI) mass spectrum, where only one fragment, arising from the loss of one alkyl side chain, is detected. This typical fragmentation characteristic may be used for diagnostic purposes in substituted TCQ derivatives. Finally, all compounds **5a–g** are highly fluorescent, as exemplified by the typical absorption and emission spectra of **5d**, presented in Figure 1. All compounds absorb at 246, 282, 322, 400, 422, 450, and 482 nm with very intense emission at 522, 563, 609, and 662 nm.

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(15) Results of this study will be published in due course.

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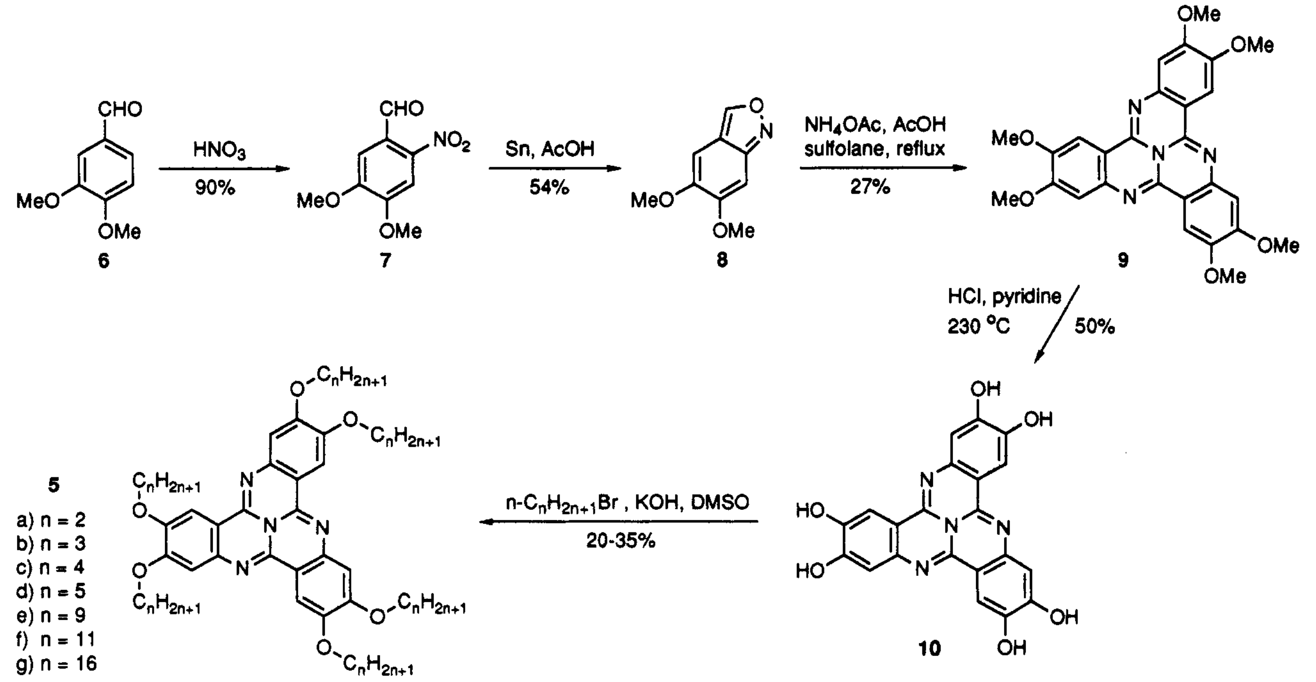
Scheme II. Synthesis of Hexa-*n*-alkoxy-TCQ, 5



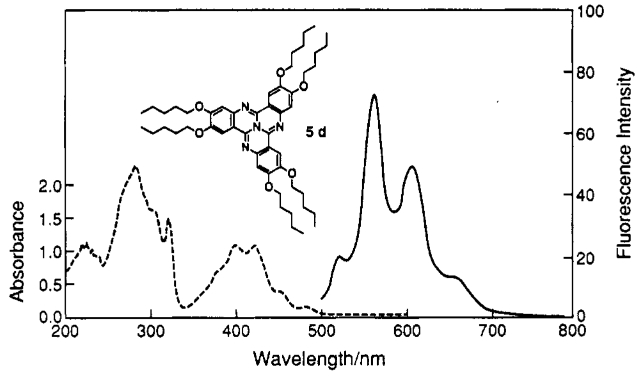


Figure 1. UV–vis absorption and fluorescence spectra of **5d**. Measurements were carried out on a Hewlett-Packard Vectra ES/12 spectrometer and a Shimadzu RF-540 spectrofluorophotometer using a 3.3×10^{-5} M solution of **5d** in chloroform. Dashed line represents UV–vis absorption. Emission spectrum (recorded upon excitation at 422 nm) is represented by the continuous line.

Compounds **5b–g** were found to be mesogenic with a very broad mesophase temperature range. The nature of these new liquid crystals was studied by differential scanning calorimetry (DSC) and by optical microscopy with polarized light. Transition temperatures and transition enthalpies were determined by DSC measurements and are given in Table I and Figure 2.

As may be seen from the data, all compounds exhibit a very similar behavior, viz. they form a single mesophase within a broad temperature range. Remarkably, the range of side chain lengths (between 3 and 16 carbon atoms) is very rare in discotic mesogens. In fact, no attempt was made to search for the upper limit of this range. It may be seen from Table I that, for the crystalline (C) to mesophase (M) transition, ΔH increases with increasing chain length. This may reflect selective melting of the side chains. Conversely, the enthalpy difference associated with the transition from the M to the isotropic liquid (I) is approximately constant, probably reflecting unstacking of the aromatic cores. The general shape of the curve showing C to M transition temperatures (Figure 2) is reminiscent of our results with the thioethers **4** and is very typical of discotic mesophases.[18]

Table I: Phase Transition Temperatures and Enthalpies of 5[a]

compd	condns	T_{SS}	T_{CM}	T_{MI}
5b (C_3)	first heating	236.6 (5.7)	286.0 (25.4)	305.6 (6.9)
	first cooling	169.0 (9.9)	259.5 (23.3)	300.6 (5.3)
	second heating	214.5 (5.6)	280.1 (19.2)	302.9 (4.9)
5c (C_4)	first heating	131.3 (7.3)	240.2 (19.2)	305.9 (3.2)
	first cooling	64.0 (6.1)	217.7 (18.4)	298.1 (4.0)
	second heating	120.0 (7.1)	238.1 (16.8)	303.2 (2.6)
5d (C_5)	first heating	144.2 (10.0)	187.8 (17.0)	301.0 (11.7)
	first cooling		154.4 (12.6)	293.5 (8.4)
	second heating		172.5 (10.1)	296.2 (8.3)
5e (C_9)	first heating		79.6 (35.7)	237.1 (6.2)
	first cooling		54.0 (34.6)	235.0 (5.4)
5f (C_{11})	first heating		71.9 (43.9)	214.7 (4.6)
	first cooling		56.3 (44.2)	208.2 (4.2)
5g (C_{16})	first heating		67.1 (84.1)	166.4 (5.6)
	first cooling		53.1 (80.0)	162.2 (2.5)

[a] Measurements were carried out on 3–5-mg samples using a Mettler TA3000 differential scanning calorimeter equipped with a TC-10A processor, heating and cooling rates being 10 °C/min. The data reflect the first heating and cooling cycle. The second heating curve is presented in cases where it appears significantly different from the first. T_{SS} = solid–solid transition temperature, T_{CM} = crystalline phase to mesophase (melting) transition temperature, T_{MI} = mesophase to isotropic liquid (clearing) transition temperature. Temperatures are given in °C and the numbers in parentheses indicate the enthalpy difference (ΔH) of transition (kJ/mol).

As exemplified by the typical DSC traces of compound **5d** and **5f** (Figure 3A and B), highly reversible behavior is observed at the clearing point of all compounds, indicating high chemical stability. Also, a very small hysteresis is observed over many heating and cooling cycles (reducing the cooling rate by a factor of five does not significantly affect the peak position). A similar behavior is observed with the melting transition, in contrast to our observations with **4** whose melting transition was found to be irreversible on the measurement's time scale.[2] Interestingly, while compounds having long side chains, **5e–g**, exhibit simple, reversible two-transitions behavior (Figure 3B), the shorter side-chain homologs, **5b–d**, show, in addition, at least one solid–solid transition prior to the

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[18] For example, see: Destrade, C.; Mondon, M. C.; Malthete, J. *J. Phys.* **1979**, *40*, C3-17.

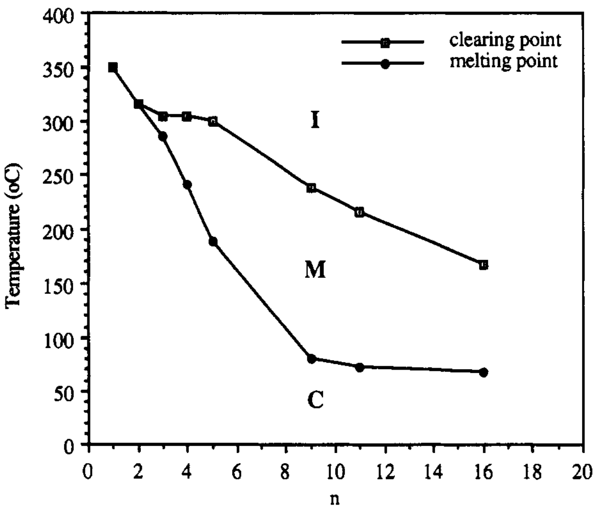

Figure 2. Phase transition temperatures of **5**. C = crystalline phase, M = mesophase, I = isotropic liquid, *n* represents the number of carbon atoms in the side chain.

melting (C to M) transition (Table I). While this solid-solid transition is reversible with **5b** and **5c**, it is irreversible with **5d**. This extra transition is observed with **5d** only during the first heating, after which all cooling and heating cycles reproducibly exhibit only melting and clearing transitions (Figure 3A), as is the case with compounds **5e–g**.

Microscopy with polarized light suggested that all compounds **5b–g** form hexagonal discotic mesophases, with essentially the same textures observed earlier with compounds **4**.[3] These optical textures are typical of highly ordered columnar mesophases.[19] Figure 4 shows three representative examples of such photomicroscopic pictures of compounds **5e–g**, obtained on cooling from the isotropic liquid. The mosaic textures, resembling reflections on steel cylinders, characteristic of an ordered hexagonal, columnar phase (D_{ho}), are very similar to those reported by Billard for 2,3,6,7,10,11-hexaalkoxytriphenylenes.[20]

X-ray diffraction studies supported the above conclusions. Figure 5 shows the X-ray diffraction pattern of compound **5f** in the mesophase. Three rings are observed near the center of the pattern, the first heavily overexposed and the second and third grainy. These can be indexed as the (10), (11), and (21) reflections from a two-dimensional hexagonal lattice with lattice constant a = 28.7 Å. In addition, two diffuse rings are found at larger distances from the center of the pattern. The first of these, centered at 4.6 Å, can be attributed to the liquid-like packing of the aliphatic chains,[21] while the second and more well-defined feature at 3.46 Å is characteristic of columnar discotics which possess stacked aromatic cores.[1,3]

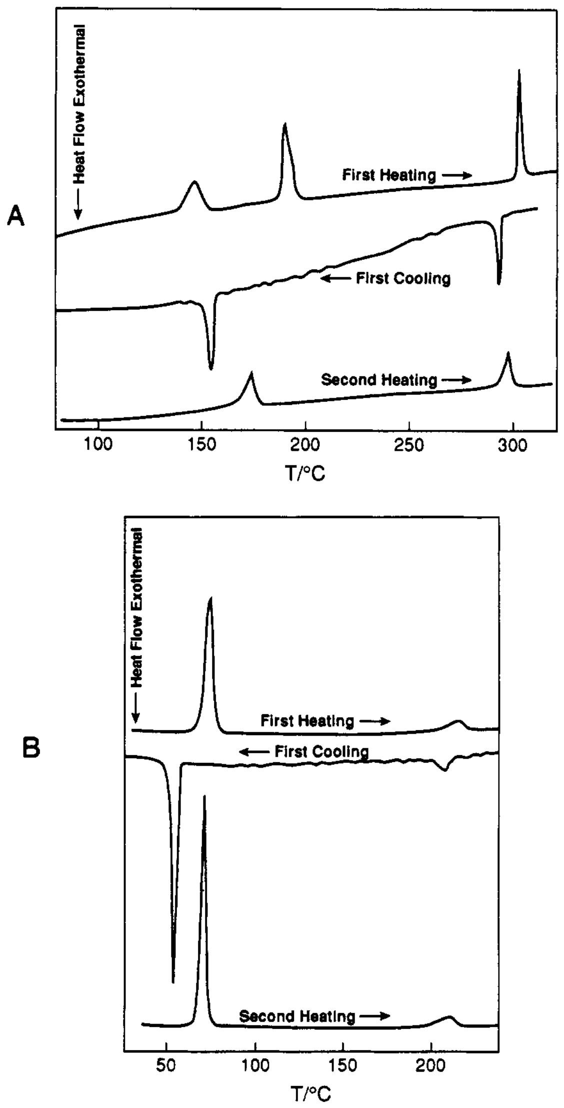

Figure 3. Differential scanning calorimetry of **5d** and **5f**. Measurements were carried out on a 3.9-mg sample using a Mettler TA3000 system equipped with a TC-10A processor, heating and cooling rates being 10 °C/min. The thermograms were obtained from the first heating and cooling cycle and second heating. A: **5d**. B: **5f**.

Similar patterns are obtained for the lower homolog **5d** in the M phase (at 197 °C), except in this case only two sharp reflections are present. These can be indexed as the (10) and (21) reflections of a two-dimensional hexagonal lattice with lattice constant a = 21.2 Å. This is the same value found for the hexagonal lattice of hexakis(thiopentoxy)TCQ described previously (compound **14c** in ref 3). The fact that the (11) and (20) reflections are not observed even after very long exposure time may be attributed to their being positioned at a minimum of the Fourier transform of the asymmetric unit. For compound **5d** the diffuse reflections occur at 4.6 and 3.46 Å.

If one assumes that the density of the compounds is near 1 g/mL, then in all cases there is one molecule per unit cell. The calculated density decreases with increasing chain length: 1.03 g/mL for **5d** and 0.90 for **5f**. Such an effect has been observed previously in similar materials.[1a,3] The corresponding values for the specific surface area per column are 2.80 × 10^7 cm²/g and 3.20 × 10^7 cm²/g.

For a hexagonal unit cell with sides a = 21.2 and 28.7 Å, and one molecule per unit cell (of compounds **5d** and **5f**, respectively), these values represent the distance between nearest neighbor columns. That distance is intermediate between the diameter of the rigid TCQ core (~14 Å)[6] and the diameter of the molecule with extended side chains, which are estimated to be 28 and 43 Å, respectively.[22] There is obviously some degree of pene-

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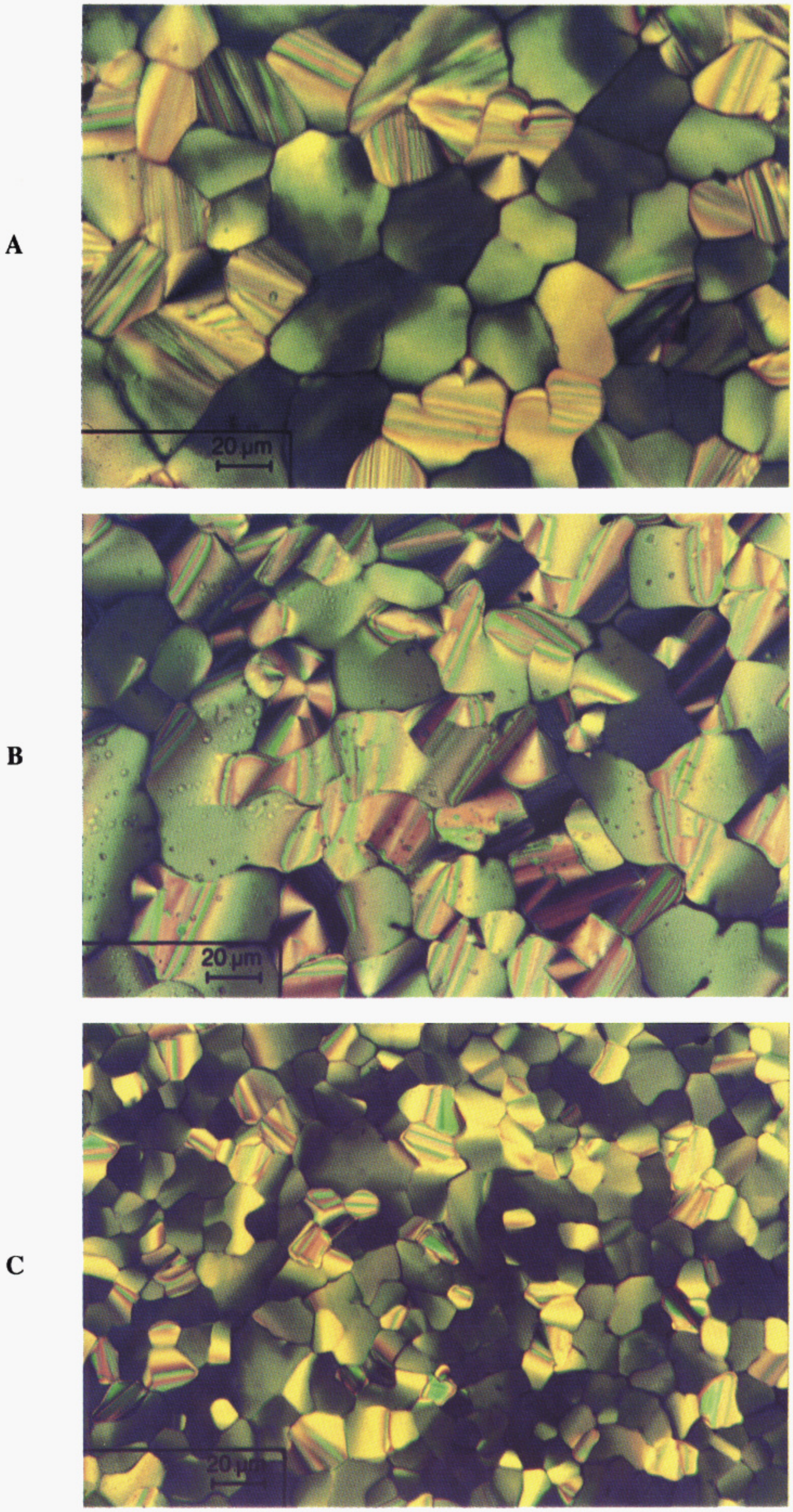

Figure 4. Optical textures of **5e–g**. Photomicroscopic pictures of the mesophase regions were obtained with a polarizing microscope (Zeiss Axiophot equipped with a Mettler FP-5 hot stage) on cooling from the isotropic liquid. A: **5e** at 125.0 °C. B: **5f** at 197.0 °C. C: **5g** at 120.0 °C.

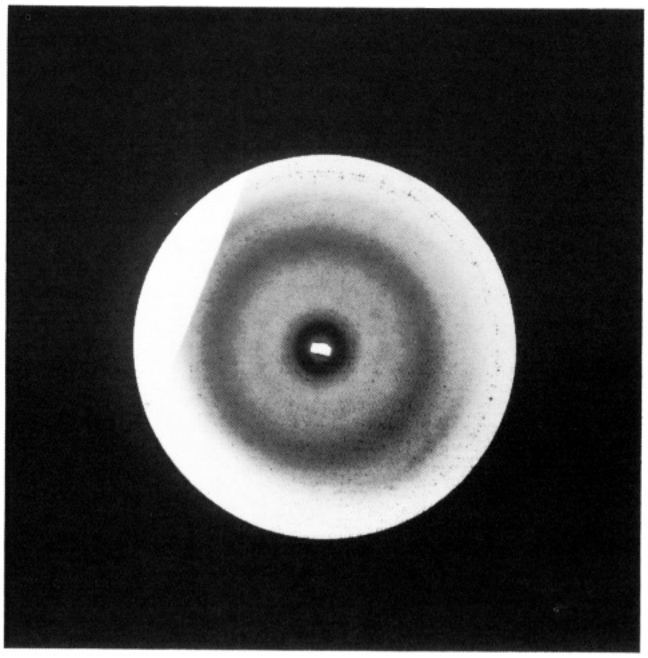

Figure 5. X-ray diffraction pattern of **5f** in the mesophase at 197 °C (±3 °C). The sample-to-film distance was 40.94 mm, and exposure time was 40 h. The spotty rings near the outer edge of the photograph are due to the calibrating salt, calcite, which coated the wall of the glass X-ray capillary. Interference from the oven windows can be observed. For more technical details see the Experimental Section.

tration of the alkyl chains into the aliphatic regions of neighboring molecules and/or orientational disorder of the alkyl chains.

In conclusion, 2,3,7,8,12,13-hexaalkoxytricycloquinazoline derivatives **5** represent a new, rather unusual family of discotic mesogens, which have C_3 symmetry and aliphatic side chains, remarkably varying from 3 to more than 16 carbon atoms, forming columnar liquid crystals over a broad temperature range. Various other potentially mesogenic TCQ and decacyclene derivatives as well as other discotic compounds with large aromatic cores are currently being investigated in our laboratories.

Experimental Section

General Methods. Elemental analyses were carried out at the Microanalysis Laboratory of the Hebrew University, Jerusalem. Melting points (uncorrected) were measured with a Mettler TA3000 system equipped with a TC-10A processor. Infrared spectra were measured in chloroform solutions with either a Perkin-Elmer 467 grating spectrometer or an FT infrared Nicolet MX-1 spectrometer, and they are given in cm^{-1}. UV–vis spectra were recorded on a Hewlett-Packard Vectra ES/12 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-540 spectrofluorophotometer. NMR spectra were measured in deuteriochloroform on a Bruker ACE-200 or a Bruker AM-400 NMR spectrometer. All chemical shifts are reported in δ units downfield from Me$_4$Si, and the J values are given in Hz. High-resolution mass spectra were determined on a Varian 711 spectrometer. Desorption chemical ionization MS was carried out on a Finnigan Mat spectrometer. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254, Art. 5549). Column chromatographic separations were performed on silica gel (Merck, Kieselgel 60, 230–400 mesh, Art. 9385) under pressure of 0.4 atm (flash chromatography). Preparative TLC was carried out on glass plates precoated with silica gel (Merck, Kieselgel 60 F-254, Art. 5717).

2-Nitro-4,5-dimethoxybenzaldehyde, 7. Nitric acid (70%, 10 mL) was cooled to 0 °C, veratraldehyde, **6** (2.0 g, 12 mmol) was added with stirring, and the mixture was brought to room temperature over 1 h and then poured into ice–water (100 mL). The resultant yellow solid was collected by filtration, washed with cold water and cold ethanol, dried, and recrystallized from 95% ethanol, affording **7** (2.3 g, 90%) in the form of yellow needles, mp 132 °C. ^{1}H NMR (CDCl$_3$): 10.43 (s, 1H), 7.60 (s, 1H), 7.41 (s, 1H), 4.01 (s, 6H). IR: 2930 (w), 2845 (w), 1685 (s), 1600 (s), 1570 (s), 1505, 1460, 1395, 1332 (s), 1280 (s), 1160, 1060, 880 cm^{-1}. MS (rel int): 211.039 (M$^+$, 21.6), 164.061 (18.8), 162.007 (17.0), 151.017 (13.3), 150.007 (14.9), 138.037 (23.4), 137.025 (15.5), 136.052 (53.6), 135.013 (14.0), 125.060 (49.0), 113.002 (23.8), 110.035 (46.0), 96.987 (34.7), 78.971 (38.9). UV chloroform, (ε, mol^{-1} cm^{-1}): 264 (18200), 350 (5300).

5,6-Dimethoxyanthranil, 8. Tin foil (1.30 g, 11 mmol) was added in small pieces to a stirred solution of **7** (500 mg, 2.37 mmol) in glacial acetic acid (15 mL), and the mixture was stirred at room temperature for 20 h and then worked up with ether and water. The organic layer was dried over anhydrous sodium sulfate, solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, hexane–ethyl acetate (8:2)) followed by recrystallization from hexane–ethyl acetate, affording anthranil **8** (230 mg, 54%) in the form of white needles. mp 110 °C. ^{1}H NMR (CDCl$_3$): 8.79 (s, 1H), 6.76 (s, 1H), 6.62 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H). IR: 2930, 2840, 1700 (s), 1568, 1495 (s), 1460 (s), 1365 (s), 1300 (s), 1270 (s), 1160 (s), 1105 (s), 1010 (s), 840 (s) cm^{-1}. MS (rel int): positive DCI, 180.0 (M + H)$^+$; negative DCI, 179.2 (100, M$^{\bullet-}$). UV: chloroform, (ε, mol^{-1} cm^{-1}): 282 (8800), 292 (8900).

2,3,7,8,12,13-Hexamethoxytricycloquinazoline, 9. Dimethoxyanthranil **8** (200 mg, 1.12 mmol) and ammonium acetate (600 mg, 7.79 mmol) were added to a mixture of sulfolane (5 mL) and acetic acid (2 mL). The mixture was refluxed for 72 h and cooled to room temperature, water was added, and the resultant greenish-yellow solid was collected by filtration, washed with water and then with methanol, and dried to give **9** (50 mg, 26.8%), mp 350 °C. ^{1}H NMR (CDCl$_3$): 7.61 (s, 3H), 6.82 (s, 3H), 3.99 (s, 9H), 3.96 (s, 9H). MS (rel int): positive DCI 501.3 (M + H)$^+$; negative DCI: 500.2 (100, M$^{\bullet-}$).

2,3,7,8,12,13-Hexahydroxytricycloquinazoline, 10. Concentrated HCl (2.2 mL) was added to pyridine (2 mL) with rapid stirring, and the mixture was heated to 220 °C to remove water. The resultant molten salt was cooled to 140 °C, hexamethoxy-TCQ, **9** (100 mg, 0.2 mmol), was added, and the mixture was heated to 230 °C for 3 h and then cooled to room temperature. Water was added, and the resultant black precipitate was collected by filtration, washed with water and with chloroform, and dried under vacuum to yield **10** (42 mg, 50%). ^{1}H NMR (MeOD): 7.31 (s, 3H), 6.54 (s, 3H); MS (rel int): positive DCI 417.1 (M + H)$^+$; negative DCI 416.1 (100, M$^{\bullet-}$).

2,3,7,8,12,13-Hexapentoxytricycloquinazoline, 5d. Powdered KOH (300 mg, 5.4 mmol) was mixed with dry DMSO (2 mL) at room temperature. Hexahydroxy-TCQ, **10** (100 mg, 0.24 mmol), and 1-bromopentane (880 mg, 2.88 mmol) were added, and the mixture was stirred at 50 °C for 4 h and then worked up by addition of water and extraction with diethyl ether. The crude product was purified by column chromatography (silica gel, hexane–ethyl acetate (9;1)) affording **5d** (70 mg, 35%) in the form of a yellow-orange solid. All other homologs, **5a–g**, were obtained in 20–35% yield using the same procedure. Their physical properties of are given below.

^{1}H NMR Data of 5a–g (CDCl$_3$). **5a (*n* = 2)**: 7.67 (s, 3H), 6.86 (s, 3H), 4.24 (t, J = 6.8, 6H), 4.17 (t, J = 6.8, 6H), 1.52 (t, J = 6.8, 18H).

5b (*n* = 3): 7.61 (s, 3H), 6.80 (s, 3H), 4.07 (t, J = 6.4, 6H), 4.03 (t, J = 6.4, 6H), 1.88 (m, 12H), 1.08 (t, J = 6.4, 18H).

5c (*n* = 4): 7.66 (s, 3H), 6.86 (s, 3H), 4.12 (t, J = 6.4, 6H), 4.09 (t, J = 6.4, 6H), 1.84 (m, 12H), 1.55 (m, 12H), 1.00 (t, J = 6.4, 18H).

5d (*n* = 5): 7.49 (s, 3H), 6.80 (s, 3H), 4.05 (t, J = 6.3, 6H), 4.02 (t, J = 6.3, 6H), 1.87 (m, 12H), 1.46 (m, 24H), 0.95 (t, J = 6.7, 18H).

5e (*n* = 9): 7.68 (s, 3H), 6.87 (s, 3H), 4.12 (t, J = 6.3, 6H), 4.09 (t, J = 6.3, 6H), 1.87 (m, 12H), 1.27 (m, 72H), 0.87 (t, J = 6.6, 18H).

5f (*n* = 11): 7.69 (s, 3H), 6.90 (s, 3H), 4.07 (t, J = 6.3, 6H), 4.04 (t, J = 6.3, 6H), 1.87 (m, 12H), 1.24 (m, 96H), 0.86 (t, J = 6.5, 18H).

Table II

compd	concn (M)	ϵ (mol^{-1} cm^{-1}) at λ_{max} (nm)						
		246	282	322	400	422	450	482
5a (*n* = 2)	4.7×10^{-5}	28 140	60 480	40 210	31 340	31 240	10 190	3340
5b (*n* = 3)	3.0×10^{-5}	35 560	75 190	47 020	34 750	34 870	10 590	3080
5c (*n* = 4)	2.3×10^{-5}	34 360	69 250	42 400	31 060	30 920	9230	2500
5d (*n* = 5)	3.3×10^{-5}	33 460	70 660	45 250	32 850	32 840	9760	2650
5e (*n* = 9)	1.3×10^{-5}	38 310	76 650	46 420	33 860	33 820	9680	2250
5f (*n* = 11)	1.9×10^{-5}	34 080	64 920	39 300	28 700	28 630	8430	2110
5g (*n* = 16)	1.3×10^{-5}	29 320	60 800	36 830	26 730	26 620	7590	1670

5g (*n* = 16): 7.60 (s, 3H), 6.77 (s, 3H), 4.08 (t, *J* = 6.3, 6H), 4.05 (t, *J* = 6.3, 6H), 1.87 (m, 12H), 1.24 (m, 156H), 0.85 (t, *J* = 6.6, 18H).

UV–vis Data. All samples were measured in chloroform. See Table II.

IR data (chloroform, the same spectrum is observed for all compounds **5a–g**): 3660 (w), 2920 (s), 2855 (m), 1625 (s), 1600 (s), 1485, 1465 (s), 1385, 1290 (s), 1100, 1000, 870 (w), 845 (w) cm^{-1}.

MS data: desorption chemical ionization, *m*/*z* (rel int)

	negative DCI $[M]^{\bullet -}$	$[M - alkyl]^-$	positive DCI $[M + H]^+$
5a (*n* = 2)	584.1 (38)	555.2 (100) $[M - C_2H_5]^-$	585.3
5b (*n* = 3)	668.4 (100)	625.4 (22) $[M - C_3H_7]^-$	669.5
5c (*n* = 4)	752.3 (20)	695.3 (100) $[M - C_4H_9]^-$	753.5
5d (*n* = 5)	836.7 (100)	765.6 (30) $[M - C_5H_{11}]^-$	837.7
5e (*n* = 9)	1172.8 (100)	1045.7 (38) $[M - C_9H_{19}]^-$	1174.0
5f (*n* = 11)	1340.9 (100)	1085.8 (32) $[M - C_{11}H_{23}]^-$	1342.2
5g (*n* = 16)	1760.9 (100)	1536.0 (20) $[M - C_{16}H_{33}]^-$	1762.7

MS data: electron impact at 70 eV, *m*/*z* (rel int). **5d (*n* = 5)**: 837 ($M^{\bullet +}$, 100), 767 (7), 708 (2), 695 (3).

5f (*n* = 11): 1341 ($M^{\bullet +}$, 100).

Elemental Analyses. 5d (*n* = 5). Anal. Calcd for $C_{51}H_{72}N_4O_6$: C, 73.17; H, 8.67; N, 6.69. Found: C, 73.25; H, 8.55; N, 6.88.

5f (*n* = 11). Anal. Calcd for $C_{87}H_{144}N_4O_6$: C, 77.86; H, 10.81. Found: C, 77.88; H, 10.65.

X-ray Studies. X-ray diffraction measurements were carried out with an Elliott GX6 rotating anode generator operating at approximately 1.2 kW with a 200 μm focus, to which was affixed a Searle camera equipped with Franks mirror optics. The Cu radiation was Ni-filtered. The powder samples were held in 1-mm glass X-ray capillaries. During each experiment the temperature of the sample was regulated with the aid of a small, homemade copper and Teflon furnace equipped with triac control. The scattering pattern was detected on Direct Exposure Film (Kodak) after an exposure time which varied from 27 to 72 h. The sample-to-film distance (approximately 40 mm) was calibrated with powdered calcite (*d* = 3.03 Å), which coated the X-ray capillary. Measurements of the reflection spacings were made directly on the films with either a steel caliper or an optical comparator.

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