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

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E. Keinan[a]; S. Kumar[a]; S. P. Singh[a]; R. Ghirlando[b]; E. J. Wachtel[c]
[a] Department of Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa, Israel [b] Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel [c] Department of Polymer Research, The Weizmann Institute of Science, Rehovot, Israel

To cite this Article Keinan, E. , Kumar, S. , Singh, S. P. , Ghirlando, R. and Wachtel, E. J.(1992) 'New discotic liquid crystals having a tricycloquinazoline core', Liquid Crystals, 11: 2, 157 — 173
To link to this Article: DOI: 10.1080/02678299208028981
URL: http://dx.doi.org/10.1080/02678299208028981

LIQUID CRYSTALS, 1992, VOL. 11, NO. 2, 157–173

New discotic liquid crystals having a tricycloquinazoline core

by E. KEINAN*†, S. KUMAR†, S. P. SINGH†, R. GHIRLANDO§
and E. J. WACHTEL‡

† Department of Chemistry, Technion-Israel Institute of Technology,
Technion City, Haifa 32000, Israel
‡ Department of Polymer Research and § Department of Organic Chemistry, The
Weizmann Institute of Science, Rehovot 76100, Israel

(Received 2 August 1991; accepted 31 August 1991)

Tricycloquinazoline, a molecule of both biological and physical interest, has been found to function as the core fragment for a remarkable new family of discotic mesogens, which have C_3 symmetry and six aliphatic side chains. Eight representative homologous 2,3,7,8,12,13-hexa(thioalkoxy)tricycloquinazoline derivatives, **14**, were synthesized, with alkyl side chain lengths varying from three to eighteen carbon atoms. These highly fluorescent, heteroaromatic compounds are conveniently obtained by nucleophilic substitution of hexachlorotricycloquinazoline, **3**, by thiolate anions. Compound **3** is prepared by trimerization of 5,6-dichloroanthranil. **12**. All compounds, **14** are mesogenic within a very broad temperature range. The nature of these new mesophases was studied by DSC, optical microscopy with polarized light, and X-ray diffraction. DSC measurements show highly reversible behaviour at the clearing point, indicating high chemical stability. Conversely, the melting transition was found to be irreversible. The diffraction spacings of three representative compounds (having 5, 8, and 18 carbon atoms in the side chain) in the mesophase are consistent, in all cases, with a two dimensional hexagonal lattice having unit cell sides of $a = 21{\cdot}2$, $24{\cdot}8$, and $34{\cdot}7$ Å, respectively and containing one molecule per unit cell.

1. Introduction

The interplay between two main factors determines the structural state of liquid-crystalline systems. On the one hand, attractive intermolecular interactions are most likely responsible for the tendency to order. The intermolecular attraction 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 hydrophobic interaction between the aliphatic side chains. Their relative importance is difficult to quantify. On the other hand, 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. One may expect that, up to some limit, increasing the attractive core–core interactions (for example by 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 recently initiated a research program focusing on the synthesis and characterization of new discogens that possess strongly interacting cores. This search has already yielded a new family of discotic mesogens, the 1,7,13-trialkanoyldecacyclenes, which form columnar liquid crystals over a broad tempera-

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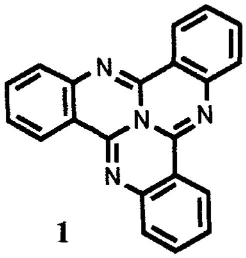
* Author for correspondence.

ture range [1]. These compounds represent a very unusual class of discotic mesogens which have C_3 symmetry and possess only three linear, aliphatic side chains.

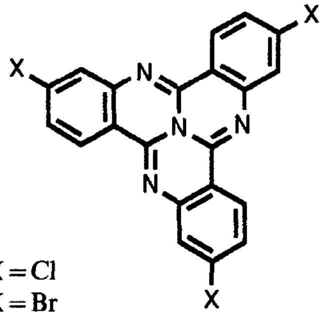
In seeking other highly interacting aromatic cores for thermotropic discogens, our attention was focused on tricycloquinazoline (TCQ), **1**, mainly because of its extraordinary thermal and chemical stability. It sublimes without decomposition at atmospheric pressure and very high temperatures, it tolerates strong oxidants such as chromic anhydride in concentrated sulphuric acid, it is highly resistant to biological oxidation [2] and, it does not couple with diazotised arylamines [3]. TCQ is readily formed in pyrolytic reactions of a number of anthranilic acid derivatives, for example methyl anthranilate [2, 4]. 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 [5]. The high carcinogenicity of TCQ, probably due to its propensity to intercalate into DNA [5 (*f*)] points to a strong tendency to stacking and aggregation, as may also be suggested by its high melting point (323°C [3, 6]) and its crystal structure [7]. This characteristic makes TCQ a particularly attractive core for discotic mesogens. In addition, this system possesses interesting conformational directionality, which arises from its C_3 symmetry [8]. Finally, TCQ exhibits intriguing physical characteristics, such as low ionization potential [9] and interesting spectroscopic properties [10], all suggesting that this system could serve as a unique core for a new family of discotic liquid crystals. In fact, except for the phthalocyanine liquid crystals [11], very few discotic mesogens having a heteroaromatic core are known.



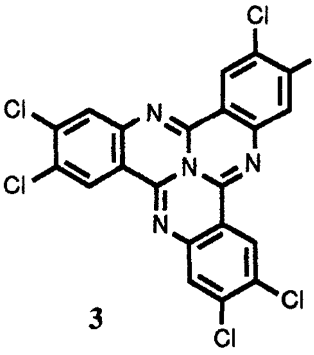
1

2. Results and discussion

Considering that the benzene rings in TCQ are highly electron-deficient (as is suggested by the remarkable resistance of TCQ to oxidation and to coupling with diazonium salts [3]), we based our synthetic strategy on nucleophilic substitution of aromatic halides. This approach required the synthesis of polyhalo-TCQ derivatives, such as 2,6,10-trichlorotricycloquinazoline **2a** and 2,3,6,7,10,11-hexachlorotricycloquinazoline **3**, as well as the corresponding tri and hexabromo analogues.



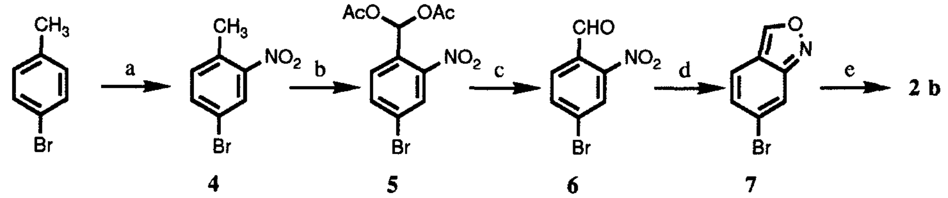
2
(*a*) X = Cl
(*b*) X = Br



3

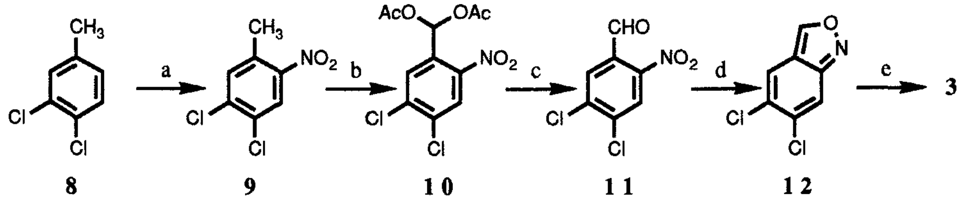
Our decision to synthesize trisubstituted TCQ derivatives from **2** and to characterize their phase transitions was based on the hypothesis that large, strongly interacting aromatic cores may form discotic mesophases even with as few as three aliphatic side chains, as was found to be the case with trialkanoyldecacyclene [1]. In addition, **2a** and **2b** are useful model substrates for studying and optimizing the nucleophilic aromatic substitution reactions of TCQ halides by oxygen and sulphur nucleophiles.

2,6,10-Trichloro-TCQ, **2a**, was prepared, as reported [6], by trimerization of 4-chloroanthranil. The synthesis of the tribromo analog, **2b** (see scheme 1) started with bromination of 2-nitrotoluene to yield 4-bromo-2-nitrotoluene **4**. The latter was oxidized with CrO_3 in AcOH to give 4-bromo-2-nitro-α,α-diacetoxytoluene, **5**, which was subsequently hydrolyzed with HCl to the corresponding aldehyde **6** [12]. Partial reduction of this nitro aldehyde to 4-bromoanthranil **7** was carried out as reported using tin foil [13]. Anthrnail **7** was successfully trimerized with NH_4OAc in sulpholane [6] to **2b**.



Scheme 1. a, AcOH, H_2SO_4, HNO_3, 0–10°C, 90 per cent. b, Ac_2O, AcOH, H_2SO_4, CrO_3, 5°C, 11 h, 61 per cent. c, EtOH, H_2O, HCl, reflux 1 h, 60 per cent. d, AcOH, Sn, room temp. 12 h, 16 per cent. e, sulpholane, AcOH, NH_4OAc, 150°C, 16 h, 35 per cent.

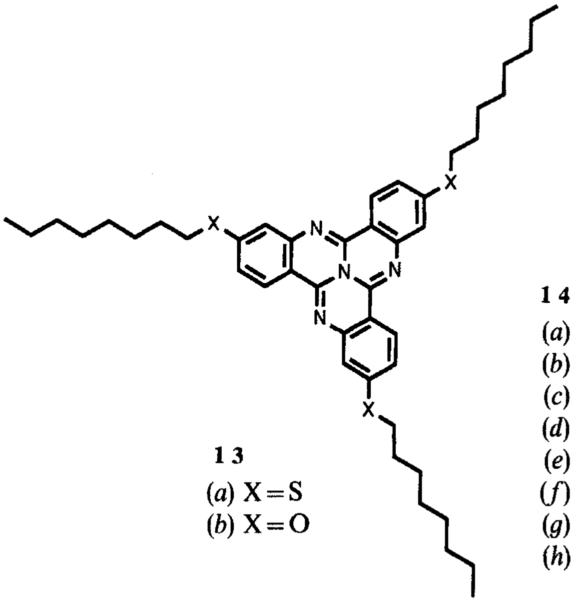
The preparation of 2,3,6,7,10,11-hexachlorotricycloquinazoline, **3** (see scheme 2), was carried out in a manner analogous to the approach described above. Nitration of 3,4-dichlorotoluene, **8**, afforded 3,4-dichloro-2-nitrotoluene, **9**. Oxidation with chromium trioxide in acetic anhydride yielded 3,4-dichloro-2-nitro-α,α-diacetoxytoluene, **10**, which was subsequently hydrolyzed to 3,4-dichloro-2-nitrobenzaldehyde, **11**. Alternatively, aldehyde **11** could be prepared directly from **9** in a single step using ceric ammonium nitrate (CAN), Partial reduction of **11** to the corresponding anthranil **12** followed by trimerization produced **3** in satisfactory yields.



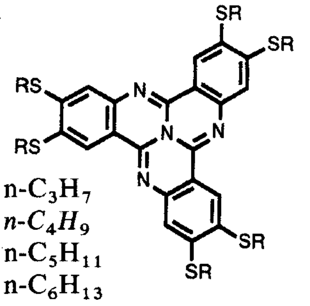
Scheme 2. a, AcOH, H_2SO_4, HNO_3, 0–5°C, 95 per cent. b, Ac_2O, H_2SO_4, CrO_3, 0–5°C, 3 h, 28 per cent. c, EtOH, H_2O, HCl, reflux 1 h, 58 per cent. d, AcOH, Sn, room temp. 20 h, 55 per cent. e, Sulpholane, AcOH, NH_4OAc, 150°C, 7 h, 40 per cent.

Having the symmetrically substituted polyhalo-TCQ derivatives **2** and **3** allowed us to study their nucleophilic substitution with alkoxides and thioalkoxides. We assumed that the electron deficiency of the benzene rings in TCQ (vide infra) would facilitate the desired aromatic nucleophilic substitution. Indeed, this was found to be a very efficient process. Reactions were typically carried out at 100°C with a primary alcohol or thiol and potassium *tert*-butoxide in either dry *N*-methylpyrrolidinone (NMP) or dry DMF under argon atmosphere. Substitution was usually complete within less than 30 min under these conditions.

Thus, treatment of either **2a** or **2b** with $CH_3(CH_2)_7SK$ in DMF at 100°C afforded 2,6,10-trithiooctyloxy-TCQ, **13a**, in 48 and 56 per cent yield, respectively. It is noteworthy that, although both **2a** and **2b** are insoluble in either NMP or DMF, they react readily with thiolates and give rise to soluble organic products. Furthermore, reaction of tribromo-TCQ, **2b** with $CH_3(CH_2)_7$ ONa in DMF/THF at 70°C using CuI as catalyst, yielded 2,6,10-trioctyloxy-TCQ, **13b**. However, trichloro-TCQ, **2a**, was found to be inert to oxygen nucleophiles under these conditions. Unfortunately, examination of the trisubstituted compounds **13a** and **13b** by differential scanning calorimetry (DSC) and by polarized light optical microscopy showed that they do not form liquid crystals. They both melt with sharp melting points to give isotropic liquids.



13
(*a*) X = S
(*b*) X = O

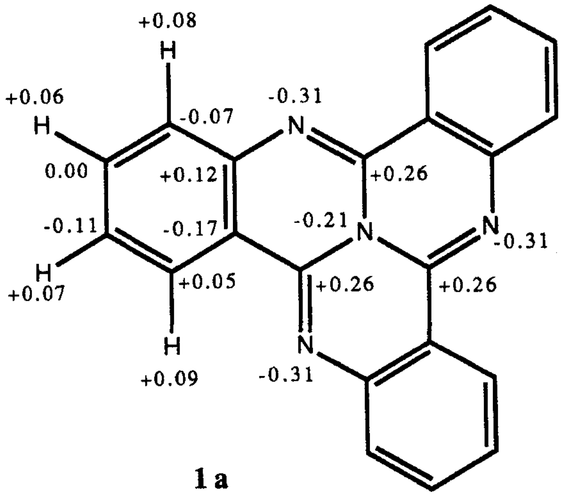


14
(*a*) $R = n\text{-}C_3H_7$
(*b*) $R = n\text{-}C_4H_9$
(*c*) $R = n\text{-}C_5H_{11}$
(*d*) $R = n\text{-}C_6H_{13}$
(*e*) $R = n\text{-}C_8H_{17}$
(*f*) $R = n\text{-}C_{12}H_{25}$
(*g*) $R = n\text{-}C_{16}H_{33}$
(*h*) $R = n\text{-}C_{18}H_{37}$

Since trichloro-TCQ, **2a**, is formed in much higher yields than the tribromo analogue, **2b**, and because substitution of either with thioalkoxides proceeds with comparable efficiency, we chose hexachloro-TCQ, **3**, to serve as our key intermediate for the synthesis of hexasubstituted TCQ compounds. Reactions were carried out under the conditions described above for substitution of **2a** and **2b**. We found, however, that with the smaller thiols, yields became significantly lower, presumably due to the increasing importance of nucleophilic dealkylation reactions, where the initially formed arylalkyl sulphide may be attacked by excess thiolate anion to produce dialkyl sulphide and thiophenolate [14]. In order to re-alkylate these exposed thiophenolate groups, we worked up the reaction mixture with the appropriate 1-iodoalkane. This modification improved the yield substantially. All products, **14a–h**, 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, and by MS and elemental analysis.

Several spectral properties of these new compounds are noteworthy. First, their very strong tendency to aggregate which, even at high dilution, can be clearly concluded from the fact that their ^1H NMR spectra are dependent on both concentration and temperature. With **14d**, for example, 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 neighbouring 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 centre of the TCQ molecule, leading to the formation of a relatively stable cation radical, localized on the nitrogen atoms. This hypothesis is supported by the general chemical properties of TCQ and by the calculated electron densities [15] shown in structure **1a**. 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.



1a

Finally, all compounds **14** are highly fluorescent, as exemplified by the typical absorption and emission spectra of **14c**, presented in figure 1. All compounds absorb at 224, 324, 348 and 430 nm with very intense emission at 572 nm.

The unique heteroaromatic structure of these compounds, which have an electron-withdrawing nucleus and an electron releasing periphery, is reflected in their chemical reactivity with respect to substitution and in their electrochemical properties. Cyclic voltametry measurements show that compounds **14** are easily and reversibly oxidized, first and second oxidation half waves ($E_{1/2}$ being 0·495 and 0·785 respectively [16].

All compounds **14a–h** were found to be mesogenic within a very broad mesophase temperature range. The nature of these new mesophases was studied by DSC, polarized light optical microscopy and low-angle X-ray diffraction. Transition temperatures and transition enthalpies were determined by DSC measurements and are given in table 1 and figure 2.

As may be seen from the data, all compounds exhibit a very similar behaviour, viz. they form a single mesophase within a broad temperature range. Remarkably, the

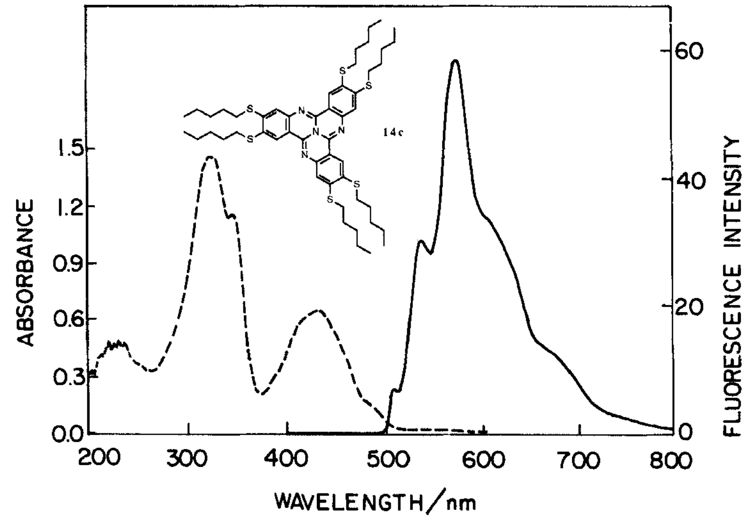


Figure 1. UV-vis absorption and fluorescence spectra of **14c**. Measurements were carried out on a Hewlett-Packard Vectra ES/12 spectrometer and a Shimadzu RF-540 Spectrofluorophotometer. UV-vis absorption (dashed line), emission spectrum (continuous line).

Table 1. Phase transition temperatures and enthalpies of **14**. Measurements were carried out on 5–7 mg samples using a Mettler TA3000 Differential Scanning Calorimeter equipped with a TC-10A processor, heating and cooling rates being 10°C min^{-1}. Data were collected from the first heating and cooling cycle: C = crystalline phase, M = mesophase, I = isotropic liquid. The numbers in parentheses indicate the ΔH of transition (kJ mol^{-1}). Numbers in italics represent transition observed on cooling.

Compound	T_{CM}/°C (ΔH/kJ mol^{-1})	T_{MI}/°C (ΔH/kJ mol^{-1})
14a (C_3)	159·7 (29·8)	274·3 (8·0)
		272·0 (7·5)
14b (C_4)	155·5 (39·9)	240·9 (7·8)
		240·8 (7·4)
14c (C_5)	113·7 (47·3)	223·2 (8·2)
		222·7 (8·0)
14d (C_6)	94·8 (52·4)	213·5 (9·7)
		210·3 (7·8)
14e (C_8)	80·7 (76·0)	207·4 (12·5)
		205·8 (11·8)
14f (C_{12})	53·9 (86·5)	170·3 (10·9)
		169·8 (10·9)
14g (C_{16})	56·5 (111·8)	152·0 (10·2)
		146·5 (10·0)
14h (C_{18})	92·2 (139·4)	183·7 (11·0)
		135·5 (9·0)

observed range of side chain lengths (between three to eighteen carbon atoms) is unprecedented in discotic mesogens. In fact, no attempt was made to search for the limits of this range. It may be seen from table 1 that, of the C to 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

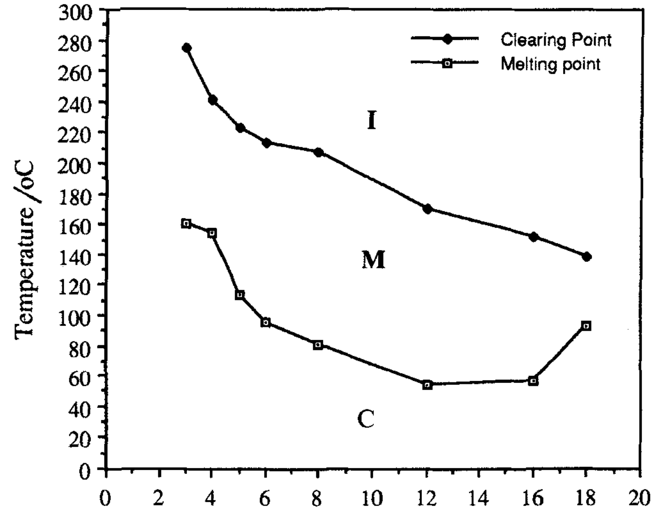


Figure 2. · Phase transition temperatures of **14**.

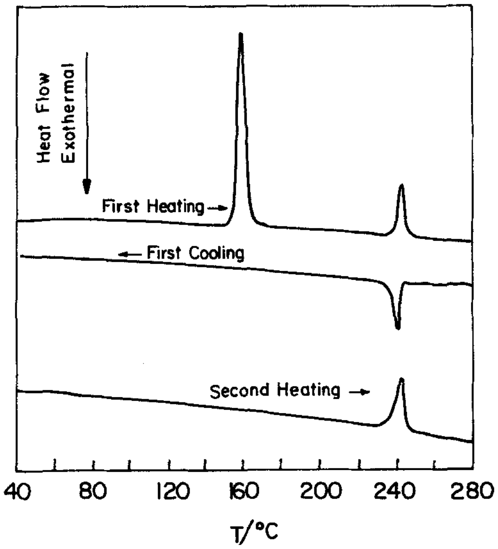


Figure 3. Differential scanning calorimetry of **14b**. Measurements were carried out on a 3·9 mg sample using a Mettler TA3000 system equipped with a TC-10A processor, heating and cooling rates being 10°C min^{-1}. The thermograms were obtained from the first heating and cooling cycle and second heating.

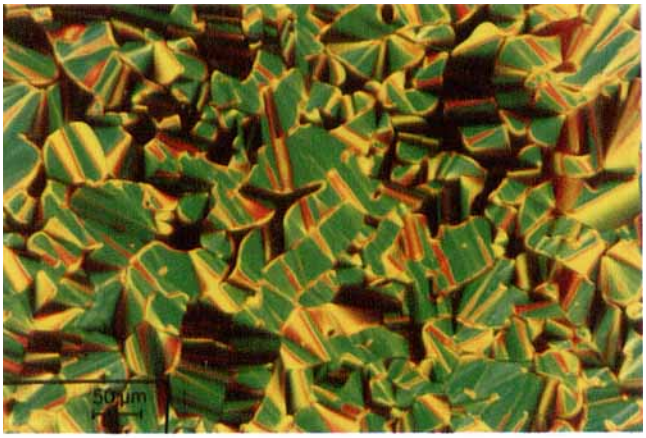
mesophase to the isotropic liquid is approximately constant, probably reflecting unstacking of the aromatic cores. The shallow minimum observed in the curve showing the C to M transition temperatures (see figure 2) is very typical of discotic mesophases [17].

Highly reversible behaviour is observed at the clearing point of all compounds, indicating high chemical stability. Also, as exemplified by the typical DSC behaviour of compound **14b** (see figure 3), a very small hysteresis is observed over many heating and

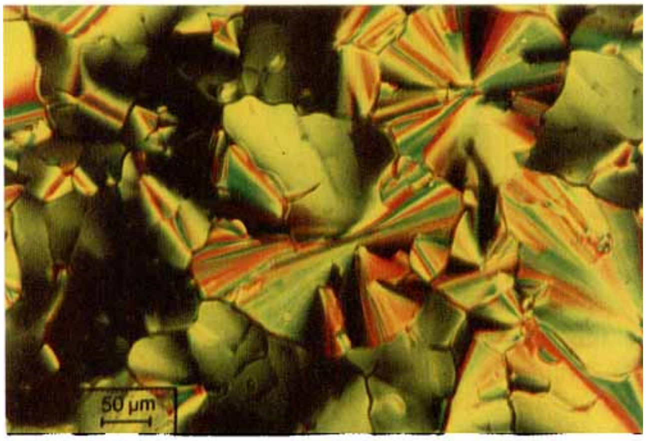
(*a*)

(*b*)

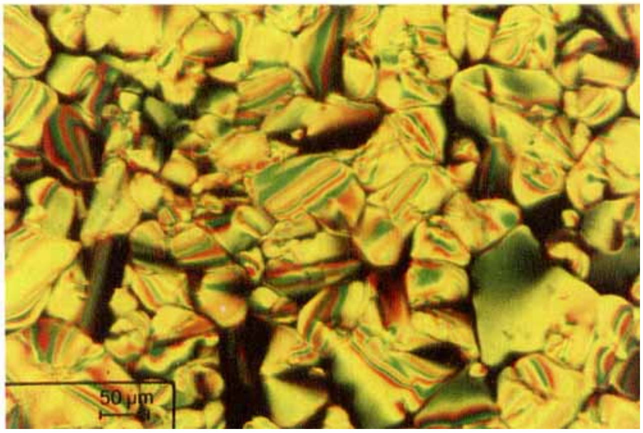
Figure 4. Optical textures of **14e-h**. Photomicroscopic pictures of the mesophase regions were obtained with a polarizing microscope (Zeiss Axiophot equipped with a Mettler FP-5 hot stage) on cooling from the isotropic liquid. (*a*) **14e** at 197·0°C. (*b*) **14e** at 197·0°C after application of pressure. (*c*) **14f** at 168·0°C. (*d*) **14g** at 122·0°C. (*e*) **14h** at 130·0°C.



(*c*)



(*d*)



(*e*)

Table 2. Observed X-ray reflections. Spacings (in Å) were measured at the temperatures indicated (vs, very strong; s, strong; m, medium; w, weak, vw, very weak). The numbers in parentheses are the Miller indices. Reflections due to the linear stacking of the aromatic cores are designated by (p) and those to the chain packing by (d).

Compound	T/°C		d/Å	Phase
14c	130	s	18·4 (10)	Hexagonal (2D) $a = 21{\cdot}2$ Å
		w	10·8 (11)	
		w	9·2 (20)	
		w	7·1 (21)	
		d	4·6	
		p	3·51	
14e	160	vs	21·7 (10)	Hexagonal (2D) $a = 24{\cdot}8$ Å
		vw	12·2 (11)	
		vw	8·2 (21)	
		d	4·4	
		p	3·37	
14h	113	vs	30·1 (10)	Hexagonal (2D) $a = 34{\cdot}7$ Å
		m	17·2 (11)	
		w	15·1 (20)	
		d	4·6	
		p	3·40	

cooling cycles. Reducing the cooling rate by a factor of five does not significantly affect the peak position. Conversely, the melting transition was found to be irreversible on the measurement's time scale (2–10° min^{-1}). Upon cooling, all mesophases turned into an amorphous, supercooled solid, with no detectable phase transition.

Polarized light microscopy suggested, and X-ray studies later confirmed that all mesophases are hexagonal discotic (vide infra). They are characterized by optical textures typical of highly ordered columnar mesophases [18]. Typical examples of compounds **14e–h**, obtained on cooling from the isotropic liquid, are shown in figure 4 (*a*), (*c*)–(*e*). For example, textures resembling reflections on steel cylinders, characteristic of an ordered hexagonal, columnar phase (D_{ho}), are shown in figure 4 (*a*). The texture shown in figure 4 (*b*) was obtained after application of pressure. These and other mosaic textures are very similar to those reported by Billard [19] for 2,3,6,7,10,11-hexaalkoxytriphenylenes.

Table 2 summarizes the X-ray diffraction spacings (d) of compounds **14c**, **14e** and **14h** in the mesophase M. In each of three cases, indexing in the mesophase is consistent with a two dimensional hexagonal lattice having unit cell sides of $a = 21{\cdot}1$, 24·8, and 34·7 Å, respectively. In the case of compound **14e**, where measurements were made at 113°C and at 160°C in both the heating and cooling directions, approximately the same results were obtained in all cases. To this extent the unit cell size does not appear to be temperature sensitive. Approximately 1 Å is added to the cell dimension per additional methylene group of the side chains. Similar results were found for the hexagonal phase of the hexaethers of triphenylene [20]. The increment is smaller than would be expected for extended, non-interleaving chains.

The diffusion reflection located at 4·4–4·6 Å (denoted d) is probably due to the liquid-like order of substituents [21]. A core-packing reflection (denoted p) consistently occurs at 3·4–3·5 Å, a value characteristic of columnar discotics having aromatic cores. This reflection is significantly sharper than that due to the chain packing and, in the compound **14c**, it is also more intense. In compound **14h**, the peak intensity ratio is reversed. If one assumes that the density of the compounds is near 1 g ml^{-1}, then in all cases there is one molecule per unit cell. The calculated density decreases with increasing chain length: 1·14 g ml^{-1} for **14c**, 1·10 for **14e**, and 0·95 for **14h**. Such an effect has been observed previously in similar materials [20]. The calculated specific surface area per column varies from $2{\cdot}5 \times 10\,\mathrm{cm}^2\,\mathrm{g}^{-1}$ to $3{\cdot}09 \times 10\,\mathrm{cm}^2\,\mathrm{g}^{-1}$, values which lie within the range observed for discotic materials [20].

For a hexagonal unit cell with sides $a = 21{\cdot}2$, 24·8, and 34·7 Å, and one molecule per unit cell (of compounds **14c**, **14e** and **14h**, respectively), these values represent the distance between nearest neighbour 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 27, 35 and 57 Å, respectively [22]. There is obviously some degree of penetration of the alkyl chains into the aliphatic regions of neighbouring molecules, and/or orientational disorder of the alkyl chains.

In conclusion, the 2,3,7,8,12,13-hexa(thioalkoxy)tricycloquinazoline derivatives, **14**, represent a new, rather unusual family of discotic mesogens, which have C_3 symmetry and aliphatic side chains varying from three to eighteen carbon atoms, forming columnar liquid crystal phases over a broad temperature range. We have recently synthesized both monomeric and polymeric discotic mesogens having 2,3,7,8,12,13-hexaalkoxy and hexaalkanoyloxy-TCQ structures [23]. 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.

3. Experimental section

3.1. *General methods*

Elemental analyses were carried out at the Microanalysis Laboratory of the Hebrew University, Jerusalem. Infrared spectra were measured in chloroform solutions with either a Perkin–Elmer 467 grating spectrometer or a Fourier transform 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 ppm downfield from Me_4Si, and J values are given in Hertz. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. 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 aluminium 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). For distillation a Büchi Kugelrohr apparatus was generally used, with the temperatures noted being pot temperatures. Tetrahydrofuran was dried by distillation over sodium benzophenone ketyl. Methylene chloride was dried by distillation over phosphorus pentoxide, dimethyl formamide by distillation from barium oxide, and dimethyl sulphoxide by distillation over calcium hydride under reduced pressure.

3.1. *Synthesis of mesogens*

4-Bromo-2-nitrotoluene **4**. A mixture of *p*-bromotoluene (103·4 g, 0·60 mol), acetic acid (48.3 g), and sulphuric acid (98 per cent, 87·6 ml) was cooled to 0°C. A mixture of nitric acid (100 per cent, 42 ml) and sulphuric acid (98 per cent, 88 ml) was added slowly over 5 h, in order to ensure that the temperature did not exceed 10°C. Upon completion the mixture was allowed to warm to room temperature, stirred for another 30 min, poured into 2 l of ice-water, and extracted with methylene chloride. The combined organic layer was washed with saturated aqueous sodium bicarbonate and dried over sodium sulphate, and the solvent was removed under reduced pressure to give crude **4** [24] in the form of a yellow oil. It was purified by absorbing the material on silica gel and washing the product out with hexane (125·7 g, 90 per cent). ^{1}H NMR (CDCl$_3$): 8·10 (s, 1 H), 7·61 (dd, *J* = 1·8, 8·2, 1 H), 7·23 (d, 1 H, *J* = 8·2), 2·55 (s, 3 H) ppm.

4-Bromo-2-nitro-α,α-diacetoxybenzaldehyde **5**. Compound **4** (39·1 g, 0·17 mol) was dissolved in 1 l of a 1 : 1 (v/v) mixture of acetic anhydride and acetic acid. The mixture was cooled to 0°C and treated with sulphuric acid (98 per cent, 150 ml). Chromium trioxide (50 g) was added very slowly over 6 h, thus ensuring that the temperature of the reaction mixture did not exceed 5°C [12]. The mixture was stirred for another 5 h at 5°C, then allowed to warm to room temperature and poured into 4 l of ice-water. The resultant solid was filtered, washed with water until the washings were colourless, then washed with 5 per cent aqueous sodium carbonate, again with water, and finally dried under vacuum to give **5** (36·5 g, 0·11 mol, 65 per cent), which was shown by TLC to be pure (EtOAc : hexane 1 : 3). ^{1}H NMR (CDCl$_3$): 8·18 (d, *J* = 1·8, 1 H), 8·11 (s, 1 H), 7·82 (dd, *J* = 1·8, 8·3, 1 H), 7·58 (d, *J* = 8·3, 1 H), 2·13 (s, 6 H) ppm.

4-Bromo-2-nitrobenzaldehyde **6**. Following the reported procedure [12] diacetate **5** (36·5 g, 0·11 mol) was mixed with water (270 ml), ethanol (50 ml), and HCl (32 per cent, 250 ml), refluxed for 1 h, and then cooled slowly to 0°C. The resultant crystals were collected and recrystallized from hexane to yield pure **6** [25 (15·1 g, 0·065 mol, 60 per cent). ^{1}H NMR (CDCl$_3$): 10·38 (s, 1 H), 8·27 (d, *J* = 8·2, 1 H), 7·93 (dd, *J* = 1·6, 8·2, 1 H), 7·85 (d, *J* = 8·2, 1 H) ppm.

4-Bromoanthranil **7**. Following the reported procedure [13] compound **6** (15·1 g, 0·065 mol) was dissolved in acetic acid (200 ml), tin foil (20 g) was added in small portions over 1 h, and the mixture was stirred at room temperature for 12 h. The product was collected by steam distillation followed by an exhaustive extraction of the distillate with ether. The combined organic layers were dried over sodium sulphate, and the solvent was removed under vacuum to yield **7** (2·0 g, 0·01 mol, 16 per cent) in the form of a yellow solid, which TLC showed to be satisfactorily pure (EtOAc : hexane 1 : 3). ^{1}H NMR (CDCl$_3$): 9·13 (s, 1 H), 7·85 (d, *J* = 0·9, 1 H), 7·48 (d, *J* = 9·2, 1 H), 7·09 (dd, *J* = 0·9, 9·2, 1 H) ppm.

2,6,10-Tribromotricycloquinazoline **2b**. Trimerization was carried out following the synthesis of **2a** [6]. Bromoanthranil **7** (11·0 g, 56 mmol) was mixed with sulpholane (125 ml), acetic acid (60 ml) and ammonium acetate (25 g). The mixture was stirred at 150°C for 16 h and cooled to room temperature; and the resultant yellow solid was collected by filtration, washed with ethanol, and dried under vacuum to give crude **2b** (3·7 g, 35 per cent). This highly insoluble material (mp > 300°C was taken to the next step without further purification. All attempts to recrystallize it failed.

4,5-Dichloro-2-nitrotoluene **9**. 3,4-Dichlorotoluene **8** (161 g, 127·9 ml, 1 mol) was dissolved in acetic acid (81 ml) and concentrated H_2SO_4 (147 ml), and the mixture was cooled to 0–5°C. A mixture of concentrated HNO_3 (70 ml) and H_2SO_4 (50 ml) was added dropwise while the temperature was maintained at 0–5°C. The mixture was stirred overnight at room temperature and poured into crushed ice, and the resultant yellow solid was filtered, washed with water, and recrystallized from hexane to give **9** [26] (195·9 g, 0·95 mol) in the form of yellow crystals. Mp 56°C. ^1H NMR ($CDCl_3$): 8·10 (s, 1 H), 7·44 (s, 1 H), 2·56 (s, 3 H) ppm.

4,5-Dichloro-2-nitro-α,α-diacetoxytoluene **10**. Concentrated H_2SO_4 (1·2 ml) was added dropwise to a solution of **9** (1·0 g, 4·85 mmol) in acetic anhydride (6 ml), the temperature being kept below 10°C. The mixture was cooled to 0°C, and a solution of chromium trioxide (1·3 g, 13·0 mmol) in acetic anhydride (6 ml) was slowly added. Stirring for 3 h at 0–5°C afforded a dark, viscous mixture, which was poured into crushed ice. The resultant yellow solid was filtered, washed with water, with aqueous Na_2CO_3 (2 per cent), and again with water. The crude product was treated with boiling hexane, cooled to room temperature, and collected by filtration. It was recrystallized from hexane–dichloromethane to give compound **14** in the form of white needles (437 mg, 28 per cent). Mp 120°C. ^1H NMR ($CDCl_3$): 8·16 (s, 1 H); 8·10 (s, 1 H); 7·77 (s, 1 H); 2·12 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): 168·0, 145·8, 138·7, 134·9, 130·6, 129·9, 127·0, 85·0, 20·4 ppm. IR: 1770 (s), 1602 (w), 1560, 1545, 1465, 1373, 1345 (s), 1183, 1140 (w), 1067, 1015 (s), 970, 910 cm^{-1}. MS (rel. intensity): 279/277/275 (M^+–NO_2, 10/47/85), 264/262 (M^+–CH_3CO_2, 10/19), 237 (9), 236 (10), 235 (57), 234 (14), 233 (100), 223 (15), 221 (92), 220 (20), 202 (10), 191 (74), 189 (84), 175 (10), 174 (14), 172 (28), 163 (13), 161 (21). HRMS: Calculated for $C_{11}H_9Cl_2O_4$ (M–NO_2): 274·9878/276·9848/278·9819. Found: 274·9876/276·9836/278·9797.

4,5-Dichloro-2-nitrobenzaldehyde **11**. Procedure A: Hydrochloric acid (3·5 N, 13 ml) was added to a solution of diacetate **10** (500 mg, 1·55 mmol) in ethanol (1·5 ml). The mixture was refluxed for 1 h and cooled to room temperature, water was added, and the product was extracted with $CHCl_3$. The organic layer was washed with water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue was recrystallized from hexane–dichloromethane to give **11** [27] in the form of white needles (197 mg, 58 per cent). Mp 69°C. ^1H NMR ($CDCl_3$): 10·35 (s, 1 H); 8·23 (s, 1 H); 8·00 (s, 1 H) ppm. IR: 3095 (w), 3005 (w), 2970 (w), 2890 (w), 1702 (s), 1595, 1555 (s), 1535 (s), 1348 (s), 1185, 1035, 948 (s), 910, 855 cm^{-1}.

Procedure B: Compound **9** (206 mg, 1 mmol) was added to a solution of ceric ammonium nitrate (4·93 g, 8·99 mmol) in 60 per cent aqueous $HClO_4$ (50 ml), and the mixture was heated to 100°C for 30 min. The solution was poured into water (50 ml) and extracted with ether (3 x 25 ml). The organic extract was washed with 2N aqueous NaOH and dried over anhydrous sodium sulphate, and the solvent was removed under reduced pressure to give an orange–yellow solid. The latter was recrystallized from hexane–dichloromethane to produce aldehyde **11** (154 mg, 70 per cent). It should be noted that substantial variations in conversion rates and yield were observed in several batches carried out according to this procedure.

5,6-Dichloroanthranil **12**. Small pieces of tin foil (1·32 g, 11·1 mmol) were added to a solution of aldehyde **11** (500 mg, 2·27 mmol) in glacial acetic acid (15 ml), and the mixture was stirred for 20 h at room temperature, then worked up with ether and water.

The organic layer was dried over sodium sulphate, the solvent was removed under reduced pressure and the crude product was chromatographed over alumina (hexane: toluene 1:1) and then recrystallized from hexane–dichloromethane to produce anthranil **12** in the form of white needles (235 mg, 55 per cent). Mp 110°C. ^1H NMR ($CDCl_3$): 9·10 (s, 1 H); 7·80 (s, 1 H); 7·73 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): 200·3, 154·7, 136·4, 129·6, 119·9, 1170, 115·9 ppm. IR: 3125, 2990 (w), 1720 (w, br), 1635 (s), 1480, 1445, 1405, 1320 (s), 1115 (s), 1090, 978, 880, 865 (s) cm^{-1}. MS (rel intensity): 191/189/187 (M^+, 12/49/63), 163 (15), 162 (64), 161 (39), 160 (100), 159 (33), 134 (23), 132 (33), 126 (18), 124 (46), 99 (29), 98 (20), 97 (77), 88 (60), 87 (29), 86 (23), 75 (16), 74 (22), 73 (33), 72 (30), 63 (24), 62 (59), 61 (72), 60 (24), 52 (17), 51 (17), 50 (23).

2,3,6,7,10,11-Hexachlorotricycloquinazoline **3**. Dichloroanthranil **12** (200 mg, 1·06 mmol) and ammonium acetate (600 mg, 7·79 mmol) were added to a mixture of sulpholane (5 ml) and acetic acid (2 ml), and the mixture was stirred at 140–150°C for 7 h and then cooled to room temperature. The resultant yellow solid was collected by filtration, washed with water, and dried under vacuum to give crude **3** (74·7 mg, 40 per cent). This highly insoluble material (Mp > 300°C) was taken to the next step without further purification.

2,6,10-Tristhiooctyloxytricycloquinazoline **13a**. (*a*) With **2a**: Potassium *tert*-butoxide (150 mg, 1·35 mmol) was mixed at room temperature with dry DMF (15 ml). Octanethiol (182·5 mg, 1·25 mmol) was added, and the mixture was then heated to 110°C in an argon atmosphere. Trichlorotricycloquinazoline, **2a** (50 mg, 0·12 mmol) was added to the hot mixture, which became homogenous within 15 min at that temperature. It was stirred for an additional 15 min and then cooled to room temperature and poured into water (50 ml). The resultant yellow precipitate was collected by filtration, washed with water and dried under vacuum. It was further purified by column chromatography (EtOAc: hexane 1:10) to give **13a** (42·6 mg, 48 per cent) in the form of a yellow solid.

(*b*) With **2b**: A reaction similar to the one described above was carried out with potassium *tert*-butoxide (300 mg, 2·7 mmol), octanethiol (365 mg, 2·5 mmol), tribromotricycloquinazoline, **2b** (100 mg, 0·18 mmol) and dry DMF (25 ml). Final purification by column chromatography afforded **13a** (49·7 mg, 56%). ^1H NMR ($CDCl_3$): 8·20 (d, $J = 8{\cdot}5$, 3 H), 7·21 (d, $J = 1{\cdot}6$, 3H), 7·10 (dd, $J = 8{\cdot}5$, 1·6, 3H), 3·01 (t, $J = 7{\cdot}2$, 6 H), 1·73 (m, 6 H), 1·28 (m, 30 H), 0·87 (t, $J = 6{\cdot}7$, 9 H) ppm. MS: Desorption Chemical Ionization, m/z (rel. intensity): Negative DCI: 752·5 $[M]^-$, 639·3 $[M\text{-}C_8H_{17})^-$; Positive DCI 753·5 $[M+H]^+$.

2,3,6,7,10,11-Hexa(thioalkoxy)tricycloquinazoline **14**. Example for procedure (*a*): preparation of **14b**. *n*-Thiobutanol (8·0 ml, 75 mmol) and potassium *tert*-butoxide (3·5 g, 31 mmol) were dissolved in dry *N*-methylpyrrolidinone (50 ml, freshly dried on a basic alumina column) under an argon atmosphere. The reaction mixture was heated to 100°C, hexachlorotricycloquinazoline, **3** (0·45 g, 0·85 mmol) was added, the mixture was stirred for 30 min, excess 1-iodobutane was added, and the mixture was allowed to cool to room temperature. It was then poured into HCl (2 M, 100 ml) and extracted with an equal volume of ether. The ether layer was washed with HCl (2 M, 2 × 50 ml) and with water and dried over magnesium sulphate. Removal of solvents (including di-*n*-butyl sulphide) under reduced pressure (70°C/1·5 mmHg) afforded a yellow-orange solid that was subjected to column chromatography on silica gel after the column had first been washed with 2·5 l hexane in order to remove trace solvents and non-polar by-products. The desired product was eluted with EtOAc : hexane (7 : 100) and recrystallized from boiling hexane to yield **14b** (63 mg, 0·074 mmol, 8·7 per cent) in the form of an orange solid. ^{1}H NMR ($CDCl_3$): 8·22 (s, 3 H), 7·15 (s, 3 H), 3·07 (t, J = 7·3, 6 H), 3·06 (t, J = 7·2, 6H), 1·80 (m, 12 H), 1·70 (m, 12 H), 1·03 (q, J = 7·3, 9 H), 1·01 (q, J = 7·3, 9 H) ppm.

Example for procedure (b): preparation of **14e**. *n*-Thiooctanol (2·5 g, 17·2 mmol) was added to dry *N*-methyl-pyrrolidinone (20 ml) under a nitrogen atmosphere. Potassium-*tert*-butoxide (1·9 g, 17·2 mmol) was added, and the mixture was stirred for 10 min at 100°C. Hexachlorotricycloquinazoline, **3** (200 mg, 36 mmol) was added, and the mixture was stirred at 100°C for 20 min, cooled to room temperature, and worked up with water and ether. The ether extract was washed with water and dried over sodium sulphate. The solvent was removed under reduced pressure, and the crude product was chromatographed over neutral alumina (hexane : ethyl acetate 95 : 5) and then recrystallized from hexane–ethyl acetate, affording **14e** in the form of yellow–orange crystals (254 mg, 58 per cent). ^{1}H NMR: 8·19 (s, 3 H); 7·12 (s, 3 H); 3·03 (t, J = 7·0 Hz, 12 H); 1·76 (m, 12 H); 1·27 (br s, 108 H); 0·84 (t, J = 6·1 Hz, 18 H) ppm.

^{1}H NMR data ($CDCl_3$): **14a** (n = 3): 8·21 (s, 3 H), 7·15 (s, 3 H), 3·03 (t, J = 7·3, 12 H), 1·80 (m, 12 H), 1·34 (q, J = 7·3, 18 H) ppm. **14c** (n = 5): 8·18 (s, 3 H), 7·11 (s, 3 H), 3·06 (t, J = 7·4, 6 H), 3·04 (t, J = 7·2, 6 H), 1·80 (m, 12 H), 1·48 (m, 24 H), 0·94 (q, J = 7·1, 18 H). **14d** (n = 6): 8·20 (s, 3 H), 7·13 (s, 3 H), 3·05 (t, J = 7·2, 6 H), 3·04 (t, J = 7·2, 6 H), 1·80 (m, 12 H), 1·54 (m, 12 H), 1·35 (m, 24 H), 0·91 (q, J = 7·1, 18 H) ppm. **14f** (n = 12): 8·17 (s, 3 H); 7·09 (s, 3 H); 3·03 (t, J = 7·0 Hz, 12 H); 1·76 (m, 12 H); 1·22 (br, s, 60 H); 0·89 (t, J = 6·1 Hz, 18 H) ppm. **14g** (n = 16): 8·14 (s, 3 H); 7·05 (s, 3 H); 3·02 (t, J = 7·0 Hz, 12 H); 1·76 (m, 12 H); 1·23 (br s, 156 H); 0·85 (t, J = 6·1 Hz, 18 H) ppm. **14h** (n = 18): 8·18 (s, 3 H); 7·11 (s, 3 H); 3·03 (t, J = 7·0 Hz, 12 H); 1·76 (m, 12 H); 1·23 (br s, 180 H); 0·85 (t, J = 6·1 Hz, 18 H) ppm.

UV-vis data: chloroform, ε ($mol^{-1}\,cm^{-1}$):

Compound	224 nm	324 nm	348 nm	430 nm
14c (C_5)	21200	61500	48200	26600
14d (C_6)	22100	69800	55400	30800
14e (C_8)	26600	71000	56400	31400
14f (C_{12})	37200	85300	67500	37000
14g (C_{16})	38700	87400	69900	40700
14h (C_{18})	31200	84800	67700	38400

IR data (chloroform, the same spectrum is observed with all compounds **14a–h**): 3670 (w), 3420 (w), 2920 (s), 2855 (m), 1615 (s), 1570 (s), 1432 (s), 1230 (m), 1095 (m), 985 (m), 865 (m) cm^{-1}.

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

	Negative DCI $[M]^{-\cdot}$	$[M\text{-alkyl}]^-$	Positive DCI $[M+H]^+$
14c	932·3 (100)	861·3 (15) $[M\text{-}C_5H_{11}]^-$	933·5
14d	1016·5 (100)	931·4 (25) $[M\text{-}C_6H_{13}]^-$	1017·7
14e	1184·6 (100)	1071·5 (23) $[M\text{-}C_8H_{17}]^-$	1185·9
14f	1520·8 (100)	1351·9 (9) $[M\text{-}C_{12}H_{25}]^-$	1521·9
14g	1857·1 (100)	1633·2 (28) $[M\text{-}C_{16}H_{33}]^-$	1857·8
14h	2026·2 (100)	1773·0 (94) $[M\text{-}C_{18}H_{37}]^-$	2026·9

MS data: electron impact at 70 eV, m/*z* (rel. intensity):

	$[M]^{+\cdot}$	$[M+1]^+$	$[M]^{+2}$	$[M+1]^{+2}$
14b	848 (54)	849 (32)	424 (7)	424·5 (3·5)
14d	1016 (20)	1017 (12)	508 (4)	508·5 (1·7)
14e	1184 (3·7)		592 (1·7)	

Elemental analysis:

14b (*n* = 4) Calculated for $C_{45}H_{60}N_4S_6$: C 63·64, H 7·12; N 6·60; Found: C 65·79, H 7·58 N 6·28.

14c (*n* = 5) Calculated for $C_{51}H_{72}N_4S_6$: C 65·62, H 7·77; N 6·00. Found: C 65·79, H 7·58 N 6·28.

3.3. *X-ray studies*

X-ray diffraction measurements were made with an Elliott GX6 rotating anode generator operating at approximately 1·2 kW with a 200 micron focus, to which was affixed a Searle camera equipped with Franks mirror optics. The Cu radiation was Ni-filtered. Prior to the experiment, the powder samples were inserted into a 1·5 mm glass X-ray capillary and briefly annealed (5–10 min) in or near the liquid phase. During the experiment the temperature of the sample was regulated with the aid of a small, homemade copper furnace equipped with triac control. The scattering pattern was detected on Direct Exposure Film (Kodak) after an exposure time of approximately 20 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 caliper or an optical comparator.

Attempts to align the materials in the mesophase by slow cooling in a 13 kG magnetic field were unsuccessful.

We thank the joint research program of the Israel National Council for Research and Development with GSF, Germany, and the Michigan Applied Research Fund (STAR) for their generous support of our program. We also thank Prof. K. Praefcke and Dr. B. Kohne of the Technical University, Berlin for helpful discussions. All MS analyses were carried out at the Mass Spectrometry Centre of Technion, Haifa.

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[15] We thank Dr. Dorit Arad of the Department of Chemistry of the Technion for providing the calculated AMPAC (MNDO) data for TCQ. More detailed calculations will be published in due course.

[16] We thank Professor J. Daub of the Institut für Organische Chemie, Universität Regensburg, Germany, for carrying out the cyclic voltametry experiments. More details on electrochemical spectroelectrochemical properties of TCQ derivatives will be published in due course.

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