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Crystal Structures of 2,3,6,7,10,11-Oxytriphenylenes. Implications for Columnar Discotic Mesophases

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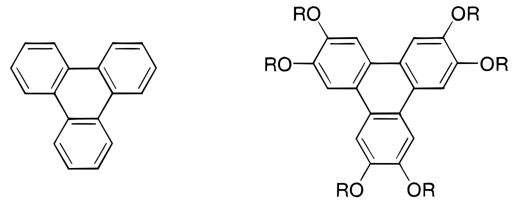
The structures of the oxysubstituted triphenylene premesogens, 2,3,6,7,10,11-hexahydroxytriphenylene (**4**), 2,3,6,7,10,11-hexamethoxytriphenylene (**5**), 2,3,6,7,10,11-hexaethoxytriphenylene (**6**), and 2,3,6,7,10,11-hexapropoxytriphenylene (**7**) were determined, and the structural results were investigated in the aim that a detailed structural knowledge of the discotic premesogens could be used to infer detailed structural knowledge with respect to known liquid crystal mesogens where little detailed structural knowledge is available. It was found that the crystal structures of the discotic premesogens were very different from the structures expected for discotic columnar behavior. These differences allowed us to shed some light on the structural forces that gives rise to the mesophasic behavior observed in such systems as being not due to stacking of the planar aromatic core as inferred hitherto but rather governed by the alkyl groups.

Introduction

The D_{3h} symmetrical molecule triphenylene **1** has interesting electronic properties and is structurally a potential discotic premesogen.(1) The term discotic is meant to imply that a rigid disk shaped polyaromatic core molecule gives rise to stacks in the structure. The disks are piling on top of one another with the vector normal to the plane of the polyaromatic core along the stacking axis. An excellent overview article dealing with the subject and terminology of discotic liquid crystals has been published.[2] Substitution of the parent molecule **1** with six alkoxy groups in a symmetrical manner in the 2,3,6,7,10,11 positions does not change the potential symmetry-related degeneracy of the molecular orbitals as demonstrated by the biradical nature of the derived dications.[3]

The interest in the mesogenic properties was spurred by the observation of "columnar discotic" mesophases with interesting dichroic behavior and furthermore these phases appeared as one-dimensional stacks of planar aromatic cores surrounded by insulating alkyl chains.[4] Such structures may give rise to exiton delocalization, conductive behavior of doped phases, and photoconductivity, and the physical properties of columnar discotic structures have been in focus for more than 2 decades.[5−8] In this regard, it is surprising that very little effort has been devoted to solving the 3-D X-ray structures of simple derivatives of 2,3,6,7,10,11-oxytriphenylenes because these structures may give important hints on the packing properties of the molecules in the interesting discotic columnar mesophases, bearing in mind that the crystal structures represent structural knowledge below the mesophase transition and that the structure of the mesophase could be very different.



1

2 (R = (CH$_2$CH$_2$O)$_2$CH$_3$)
3 (R = (CH$_2$)$_4$CH$_3$
4 (R = H)
5 (R = CH$_3$)
6 (R = CH$_2$CH$_3$)
7 (R = CH$_2$CH$_2$CH$_3$)

Figure 1. Parent molecule **1** and the molecules subject to discussion and study in this paper.

The structure of the parent molecule triphenylene **1** has been solved by X-ray,[9] neutron[10] and even electron

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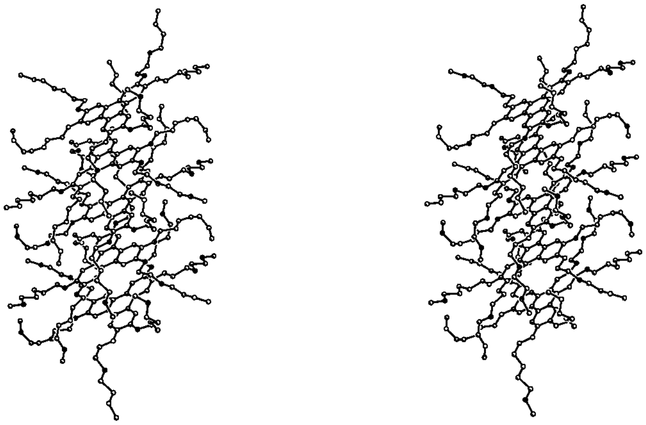

Figure 2. Columns of slipped stacks observed in compound **2**. It is noticeable that while the structure is columnar it does not appear discotic and the degree of aromatic overlap is limited. The illustration was generated from the data (ref 12) available within the CCDC database.

diffraction.[11] The packing motif is characterized by slipped stacks of the planar molecules with the trichotomous molecular structures repeated with a simple translation. The structure of 2,3,6,7,10,11-hexakis(1,4,7-trioxaoctyl)triphenylene (**2**) has been published, and in that material, the pattern is dominated by slipped stacks of the planar cores with the trichotomous pattern of ethyleneoxy chains repeated with inversion between adjacent molecules. While the structure is columnar it is worth noting that the mesogenic molecule in that structure does not appear "discotic" as shown in Figure 2 where slipped stacks of molecules are observed.[12]

A similar packing pattern for the columnar phases was inferred from synchrotron X-ray studies of suspended strands of hexadodecanoateesters of compound **4**[13] in the hexagonal mesophase. Interestingly, sparse crystallographic data on this series of compounds albeit with shorter chain length has been published,[14] and the data were found to give rise to staggered dimers of the mesogenic core molecules. In the case of the hexaalkylthiotriphenylenes, an extensive study by Heiney et al.[15] on hexahexylthiotriphenylene showed that the structure in the crystalline phase was in fact consisting of eclipsed stacks with no slip of the mesogenic molecules.

Earlier X-ray powder patterns of columnar mesophases have been interpreted as arising from columns of eclipsed or staggered dimers[16,17] and models for that arrangement and its potential disorder have been discussed.[18] TEM and model calculations[19] have been used to elucidate the structure of 2,3,6,7,10,11-hexapentyloxytriphenylene (**3**). Also calculations have been employed in order to gain insight in the packing patterns of triphenylene mesogens.[20,21]

We have prepared single crystals of 2,3,6,7,10,11-hexahydroxytriphenylene (**4**) monohydrate, 2,3,6,7,10,11-hexamethoxyoxytriphenylene (**5**), 2,3,6,7,10,11-hexaethoxytriphenylene (**6**), and 2,3,6,7,10,11-hexapropoxytriphenylene (**7**) ethyl acetate solvate and determined their structure. The structural results are discussed in terms of the understanding of discotic phases based on the literature.

Experimental Section

Preparation of Compounds. Well-formed crystals of compound **4** were obtained as the stable monohydrate by recrystallization from water.[22] Single crystals of 2,3,6,7,10,11-hexamethoxytriphenylene[23] (**5**) and 2,3,6,7,10,11-hexaethoxytriphenylene[21] (**6**) were obtained by sublimation at 270 °C in a vacuum (2×10^{-2} mbar). 2,3,6,7,10,11-Hexapropoxytriphenylene[24] (**7**) EtOAc crystals were obtained by recrystallization from ethyl acetate. Attempts to obtain solvent-free single crystals of compound **7** by sublimation failed.

Crystal Structure Determinations. Suitable single crystals of **5** and **6** (obtained by sublimation) were mounted on glass fibers using epoxy glue. Crystals of **4** and **7** lost solvent upon exposure to air. Therefore, they were drawn directly from the mother liquor, coated with a thin protecting layer of oil, mounted on a glass fiber using Apiezon grease, and transferred quickly to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer (Siemens SMART CCD Platform). An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames; each set with a different φ angle for the crystal and each frame covering a scan of 0.3 ° in ω. Data collection, integration of frame data and conversion to intensities corrected for Lorenz, polarization and absorption effects were performed using the programs SMART,[25] SAINT,[25] and SADABS.[26] Structure solution, refinement of the structures, structure analysis and production of crystallographic illustrations was carried out using the programs SHELXS97,[27] SHELXL97,[28] PLATON,[29] and SHELXTL.[30] In all of the structures, H atoms were included and their positions refined. A summary of crystal data, X-ray data collection parameters and structural refinement results is given in Table 1. The structure analyses of **4** and **5** did not involve any problems. Several attempts to collect data on crystals of **6** at 120 K failed. Every crystal produced an X-ray pattern which could not be assigned to a reasonable unit cell. It turned out, however, that data could be collected at room temperature and also at lower temperatures down to about 175 K. The resultant displacement parameters for the ethyl carbon atoms are very large at room temperature and suggest some disorder, which, however, could not be modeled properly.

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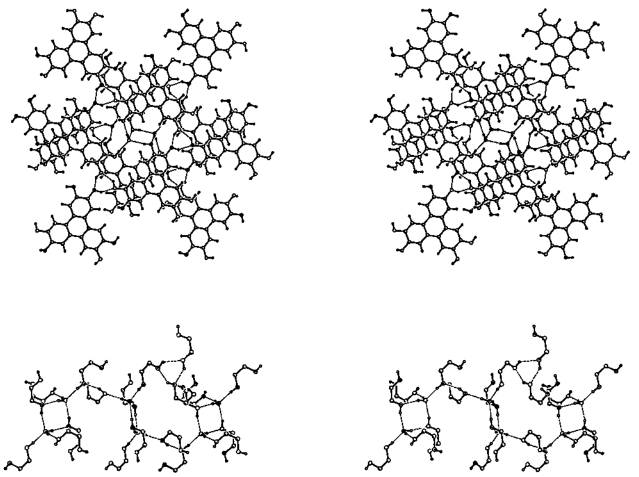

Figure 3. Stereoview of the structure of **4** showing the specific hydrogen interactions. Notice the two different networks that are observed: one closed ring network and one that extends throughout the structure (above). Close-up stereoview of the networks involving specific hydrogen interactions. The closed ring network is seen in the upper left part of the drawing while the extended network is seen from right to left (below).

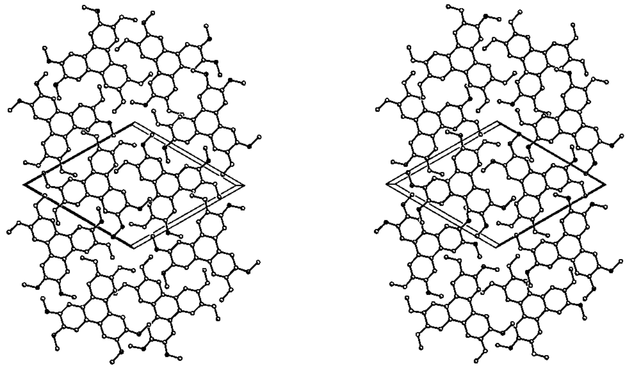

Figure 4. Stereoview of the structure of **5** as a projection along the *c* axis. The important point is that the molecules do not stack and that no aromatic overlap is observed. The molecules pack in planes with the methyl groups of one molecule above the aromatic part of neighboring molecules.

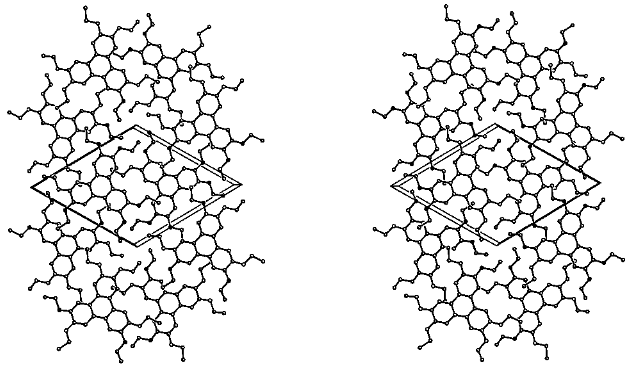

Figure 5. Stereoview of the structure of **6** as a projection along the *c* axis. The structure of **6** is isostructural with that of **5**. The alkyl groups are however more crowded above the aromatic planes.

More reasonable parameters were derived from the structure determination at 180 K. A data collection at 175 K was also carried out, but the structure could not be refined to an *R* value below 0.20 and it is therefore not reported in detail. The structure determination of **7** was complicated by disorder of the solvent ethyl acetate. This molecule is situated around a site with a higher symmetry than the molecule, and the molecule has thus been evenly distributed on several symmetry equivalent orientations. The bond lengths and bond angles as well as atomic coordinates and further experimental details have been deposited.[31]

Differential Scanning Calorimetry (DSC) Measurements on Compound 6. DSC data were recorded on a PYRIS 1 instrument from Perkin-Elmer. Compound **6** (16.540 mg) was sealed in the sample container and subjected to the measurements. Several scans (up and down in temperature) were made between 100 and 533 K at scan rates of 10 K and 20 K min^{-1}. A complex phase transition was observed in the range 170−210 K consistent with the X-ray experiments, and apart from melting, no other transitional behavior was observed. The DSC data around the phase transition are shown in the lower part of Figure 6.

Results and Discussion

Structural Descriptions. The structure of the parent aromatic core, triphenylene, has been known for nearly 4 decades and has been studied by various diffraction techniques (X-ray, neutron, and electron diffraction[9−11]). The structure is what would be termed a typical structure for a large planar aromatic system as it exhibits the herringbone packing pattern well-

Table 1. Crystal Data and Structure Refinement Parameters

compound	**4**	**5**	**6**	**6**	**7**
formula	$C_{18}H_{12}O_6{\cdot}H_2O$	$C_{24}H_{24}O_6$	$C_{30}H_{36}O_6$	$C_{30}H_{36}O_6$	$C_{36}H_{48}O_6{\cdot}C_4H_8O_2$
M	342.29	408.43	492.59	492.59	608.81
T/K	120(2)	120(2)	294(2)	180(2)	120(2)
cryst syst	monoclinic	hexagonal	hexagonal	hexagonal	cubic
space group	$P2_1/c$	$P6_3/m$	$P6_3/m$	$P6_3/m$	$Fd\bar{3}c$
a/Å	11.127(2)	13.1240(13)	14.391(2)	14.482(2)	30.211(4)
b/Å	12.797(3)	3.1240(13)	14.391(2)	14.482(2)	30.211(4)
c/Å	11.081(2)	6.8481(7)	7.2820(15)	7.0838(2)	30.211(4)
α/deg	90	90	90	90	90
β/deg	119.32(3)	90	90	90	90
γ/deg	90	120	120	120	90
V/Å^3	1375.9(5)	1021.49(18)	1306.1(4)	1286.6(4)	27573(6)
Z, D_x/(g cm^{-3})	4, 1.652	2, 1.328	2, 1.253	2, 1.271	32, 1.173
λ/Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
μ/mm^{-1}	0.129	0.095	0.086	0.087	0.078
cryst size/mm	0.13 × 0.08 × 0.05	0.22 × 0.13 × 0.13	0.35 × 0.11 × 0.09	0.35 × 0.11 × 0.09	0.25 × 0.20 × 0.20
no. of measd reflcns	14057	10607	13739	13283	64250
no. of unique reflcns	2786	759	961	952	1200
R_{int}	0.0357	0.0414	0.0743	0.0978	0.1912
no. of reflcns with $I > 2\sigma(I)$	2185	605	462	588	780
R (F, $I > 2\sigma(I)$)	0.0385	0.0363	0.0588	0.1182	0.0637
wR (F^2, all)	0.1093	0.1057	0.1979	0.3394	0.2062

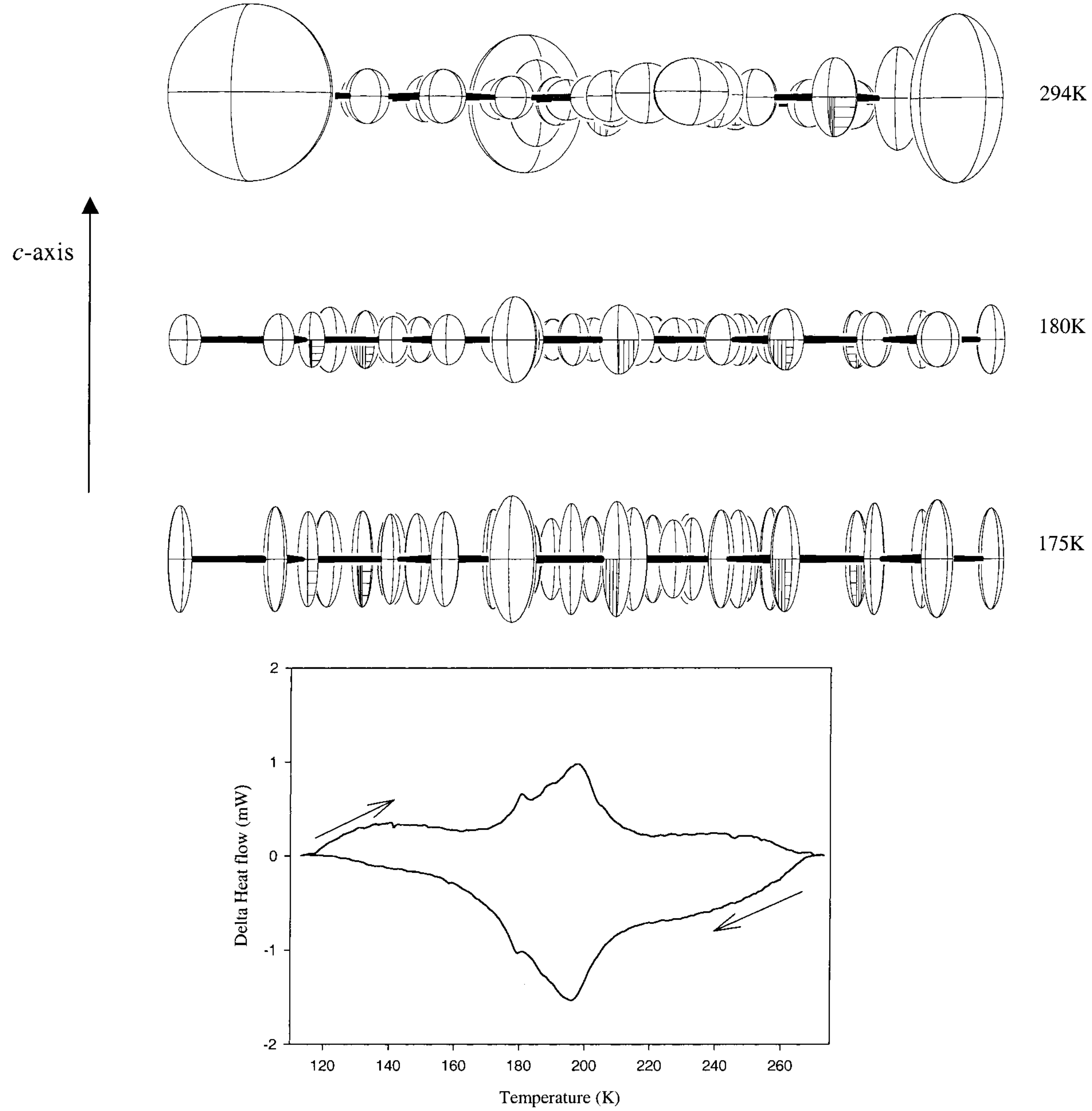

Figure 6. ORTEP drawings of **6** at the three different temperatures (294, 180, and 175 K) at which the structure was determined. The molecules are seen from the side, and it is seen that the thermal displacement parameter along the *c* axis decreases on cooling from 294 to 180 K but increases on cooling further from 180 to 175 K. This is suggestive of some mechanism other than a thermal one taking place, perhaps an order/disorder mechanism (above). The DSC traces (arrows indicate the thermal gradient) for cooling followed by heating in the temperature interval 160 and 273 K showing the complex nature of the phase transition where the largest changes are observed in the temperature range 170−210 K.

known to these compounds.[32] Most liquid crystals based on the triphenylene system are based on various alkylated and alkanoylated forms of 2,3,6,7,10,11-hexahydroxytriphenylene (**4**). The structure of **4** differs in many ways from its parent compound triphenylene, primarily due to the hydroxy substituents but also due to specific hydrogen interactions between molecules and between molecules and solvent water.

This leads to the molecular planes being arranged in layers with incomplete overlap between molecules in adjacent layers; however, the molecular orientation is eclipsed rather than staggered as observed for **1**. There are six hydroxy groups on each molecule of **4** allowing for in principle 18 different specific hydrogen interactions (six as donor and 12 as acceptor). Further, there is one water molecule allowing for four different specific hydrogen interactions (two as donor and two as acceptor). In **4** five of the OH bonds are in the plane of the molecule and one is out of plane with the molecular plane. The specific hydrogen interaction networks could be classified using graph theory[33−36] using the formal-

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(31) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (international) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk] on quoting the depository numbers CCDC-147348, CCDC-147349, CCDC-147350, CCDC-147351, and CCDC-147352.

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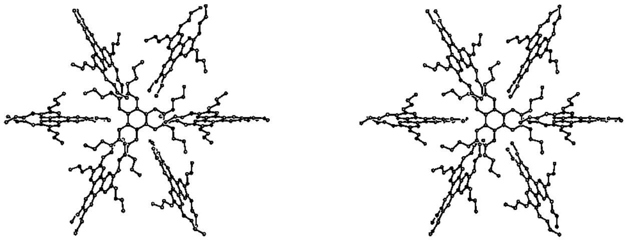

Figure 7. Stereoview of the packing in **7** where the scissoring of the alkyl chains leads to a structure with a very unusual space group and with planes of the aromatic molecules at near right angles to one another.

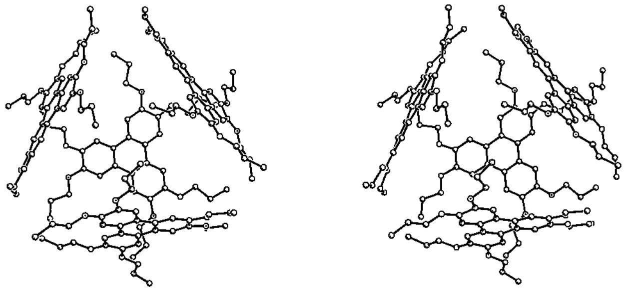

Figure 8. Stereoview of the pocket with a tetrahedral geometry formed between the molecules of compound **7**. The disordered ethyl acetate molecules reside in these pockets.

ism developed by Etter. Three distinct types of motif were observed. And these were observed in two different networks. One network was a closed ring that does not extend throughout the crystal and consists of only one motif and involves three of the hydroxy groups on **4**, which could be assigned as $R_3^3(6)$. The second network extends throughout the crystal and involves both solvent water and the remaining three of the hydroxy groups on **4**. The network consists of larger rings interconnected by chains. The ring could be assigned as $R_4^4(8)$ and the chain as $C_3^3(6)$. The solvent water is situated in the crystal with a tetrahedral coordination and links the two graph sets.

The space group symmetry does not reflect the high molecular symmetry neither for triphenylene nor for compound **4**. Compound **5** however does this, and it has a packing which also differs significantly from our preconception of columnar discotic packing. In fact the complete opposite is observed with as little aromatic overlap as possible.

This can however be rationalized by the quite rigid conformation of the molecule and by the fact that the observed packing pattern gives rise to efficient space filling with the methoxy groups occupying the space left by the aromatic part (remembering that the shortest intermolecular distances are 3.3 and 4.6 Å, respectively, for stacks of aromatic molecules and alkyl chains).

In lengthening the alkyl substituent by one carbon each, thus obtaining **6**, the same structure (as for compound **5**) is observed at room temperature and down to 180K.

On cooling further, a phase transition probably takes place or perhaps a severe order−disorder transition. This is evidenced by the fact that the structure could be solved at 175 K but only with great difficulty, and as shown in the figure the anisotropic displacement parameters along the *c* axis become extremely large, suggesting that the some mechanism other than a thermal one is taking place.

Moving to the next molecule in the series, compound **7**, where the number of alkyl chain carbon atoms exactly matches the number of aromatic carbon atoms, a new type of solvent containing structure is observed that belongs to a for organic molecules very rare space group. In this structure (Figure 7), the molecules no longer pack in planes. Instead the planes of the aromatic units are at near right angles to each other with the scissors shape formed by two adjacent propoxy groups packing together.

The voids thus created are filled by the disordered solvent ethyl acetate molecules. The voids essentially have tetrahedral geometry and the aromatic cores are on the faces of this tetrahedron (Figure 8).

The scissoring also leads to a slight twist of the otherwise planar molecular system. A comparison of the four molecules are shown in Figure 9. It is noteworthy that the direction in which the growing alkyl chain extends is the same for all the molecules suggesting that the first part of the chain is quite rigid. This has also been noted for hexaalkylthiotriphenylene where the chain stiffness is dominant in both the crystalline and the first mesophase ($\mathbf{D_{ho}}$).[15]

On the basis of the short chain compounds, it would thus seem that when the number of alkyl carbons becomes dominant they dictate the structure and when the aromatic carbon atoms are dominant the alkyl carbons still influence the structure heavily, and in essence, the aromatic core is a very weak structure generator that only serves to fix the starting point of the alkyl chains in space.

Structural Impact on Our Understanding of the Known Mesophases. Our most important observation by inspection of the determined structures of the simple compounds **4**−**7** is that they bear no resemblance to the columnar mesophases. Intuitively one expects small molecules with planar aromatic cores to stack. It should however be remembered that eclipsed π stacking is basically repulsive. The major effect in the compounds examined seems to stem from the different space filling properties of alkyl chains and planar aromatic cores, where typical repeat distances are 4.6 and 3.3 Å respectively, the latter taken as a characteristic interplanar distance in stacked unsubstituted aromatics. In compounds **4**−**6**, space filling is best obtained by accommodating the pendant chains over the aromatic cores (Type 1 packing). Propoxy chains in compound **7** appear to be too long and type 1 packing is no longer possible and an exotic solvate structure appears. It seems reasonable to assume that packing of oxytriphenylenes bearing pendants longer than C_4 will adapt a packing motif similar to compound **2** (Type 2) or appear as eclipsed or staggered dimers or higher aggregates with more or less disorder along the columnar structure.[18]

Our main result is thus that one should examine in detail the spacefilling properties of discotic mesogens if the desire is to obtain columnar materials with exten-

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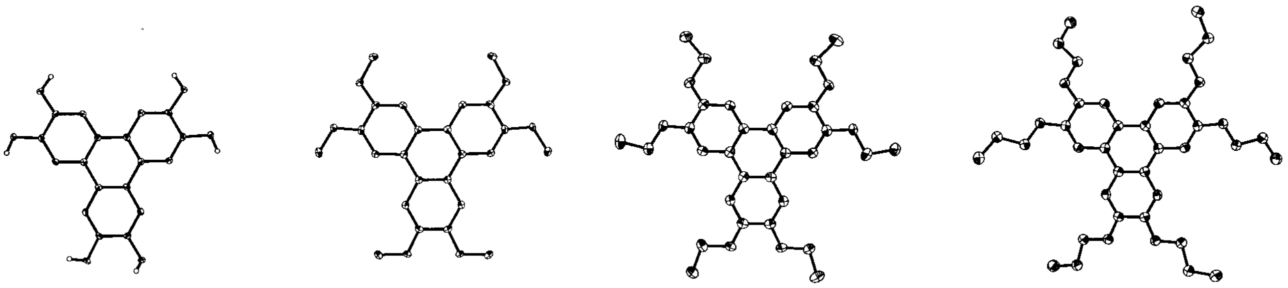

Figure 9. ORTEP drawings of the four molecules investigated in this study. Hydrogen atoms on the hydroxy groups of **4** have been included all other hydrogen atoms have been omitted. The important point is that the direction in which the alkyl groups extend is identical for compounds **5**−**7**, which indicate that the chains are rigid.

sively delocalized π systems. We are however aware that the structure may change to produce π stacking even for short chain derivatives of oxytriphenylenes when they are doped or extensively oxidized to cation radical salts[6] in line with that the main effect upon oxidation is that the $\pi-\pi$ interaction can become bonding.

Conclusions

The structure of triphenylene-based liquid crystal mesophases has been subject to intense study and discussion. Despite the very limited detailed structural knowledge on these systems some audacious propositions as to the structural nature of these compounds have been made. While the experimental evidence indicates a columnar structure it is tempting to imagine the columns as arising from stacks of the molecules which are shaped like disks and therefore, conceptually at least, are expected to stack like discs, the disc shape being the structure generator. The term discotic has been applied to describe this packing behavior. However, recent crystal structural data shows such a columnar phase as being formed from slipped stacks of individual molecules. This prompted us to investigate this behavior by solving the structures of four different compounds pertaining to triphenylene. On the basis of the structural changes observed as the substituent chain length was increased, it became evident that the main factor that governs the structural outcome is the substituent alkyl chains and not as perhaps implied hitherto the aromatic core mesogen.

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