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Core-halogenated, helical–chiral triphenylene-based columnar liquid crystals†

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(*Received 23 August 1996; accepted 22 October 1996*)

It is shown that chlorination and even bromination of the mesogenic hexahexyloxytriphenylene **1** can take place at the sterically congested tetracyclic core delivering the respective mono-halogenated, sevenfold substituted enantiotropic mesogens **3** and **4** in 32 and 17% yields, respectively, giving mesophases over greater temperature ranges. Miscibility tests among all mesogenic compounds of this study prove formation of the columnar hexagonal type of phase. The steric and electronic effects of those substituents, different from the six equal alkoxy groups, on the mesophase are discussed in detail. In our hands and to our surprise, the sterically hindered acceptor (nitro or halogeno) substituents of **2**, **3**, or **4** could not be replaced by an alkylthio group in nucleophilic aromatic substitution reactions using the aprotic polar solvent DMEU. Semi-empirical calculations on numerous hexaethers with one or two substituents, e.g. halogens or others, in one of the three bay regions of the triphenylene core reveal that these molecules are helically deformed due to the crowding in the molecule. In this new case of atropisomerism, the 1,12-disubstituted derivatives should offer the possibility of resolution into enantiomers and, therefore, of studying disc-like mesomorphic compounds possessing for the first time the origin of chirality within their molecular centre.

1. Introduction

One of the best and longest studied families of flat monomeric and polymeric thermotropic liquid crystals is derived from triphenylene carrying (apart from some exceptions synthesized only in recent times [2–4] *six* chalcogeno-bridged [5–7] flexible carbon chains in which oxygen is by far the commonest. Recently, however, 2,3,6,7,10,11-hexa-alkyl*thio*-derivatives already introduced by us some time ago [6] have become the centre of scientific attention and intensive research owing to their pronounced photoconductivity [8].

In view of this promising situation and that a homologous *N*-acyl series (ten members) of '*seven* tail' triphenylene-based liquid crystals was first published recently [3] which, compared to the parent 2,3,6,7,10,11-hexaethers of triphenylene [2, 5 *(a)],* show, in spite of their twisted conformation, strongly improved thermomesomorphic properties [3], we renewed our long standing interests in sulphur- and selenium-containing mesogens [6, 7] possessing this important aromatic core system, seeing now the possibility of developing from it for the first time helical–chiral columnar liquid crystals. Our recent results on this new topic are presented here.

2. Experimental

2.1. *General*

The chemical structures of all final products were confirmed by standard spectroscopic methods: ^{1}H, including NOE-experiments, and ^{13}C NMR spectroscopy (400 and 270 MHz, respectively, solvent: $CDCl_3$), as well as mass spectrometry (MS, Varian MAT 711, 70 eV, 210–300°C, direct inlet) including high resolution (h.r.) of the M^+ peaks. Only characteristic data are selected from these spectra and quoted later.

The products of each reaction stage were purified by flash chromatography (column diameter 52 mm, silica gel 60, grain diameter 40–63 microns; elution with mixtures of light petroleum (l.p., boiling range 30–70°C) and dichloromethane (dchm.) as described elsewhere [9]. The purity of the compounds prepared was checked by thin layer chromatography using Merck 60 F254 preformed aluminium-backed plates. Each of our final products was found by DSC (see below) to have a chemical purity in excess of 99·4 mol %.

The phase assignments and initial transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope (PM, Leitz Laborlux 12 Pol) in conjunction with a hot stage and controller (Mettler FP82 microfurnace and FP80 control unit). Also, differential scanning calorimetry (DSC, Mettler TA 3000/DSC-30 S with TA 72·5 software) was

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† Part 105 on liquid crystalline compounds; for part 104 see [1].

used to confirm the transition temperatures observed by PM and to measure the enthalpies of these phase transitions.

Quotations of the temperatures (°C) obtained by these two methods (PM or DSC) and of the enthalpy values (kJ mol^{-1} in brackets) in this Experimental part are made in the following order: PM/DSC (ΔH); Cr = crystalline; Col$_h$ [10] = columnar hexagonal; I = isotropic liquid, RT = room temperature.

Our calculations of the conformations of the three acceptor-substituted triphenylene hexaether models shown in figure 1 were performed using the semi-empirical MNDO94 3·0/AM1 procedure with the standard parameter set of the Unichem 3·0 software package (Cray Research Inc.) on a Cray J 932/16-8192 computer; SCF field consistency was achieved in each case. Furthermore, the energy barriers for the racemization of eleven hexamethoxytriphenylene derivatives were calculated using the MOPAC-7 program on an IBM RS/6000-320H work station.

2.2. *1-Nitro-2,3,6,7,10,11-hexahexyloxytriphenylene* (**2**) [2, 11]

Following a published procedure [2], the nitration of 2,3,6,7,10,11-hexahexyloxytriphenylene (**1**) [10·78 g, 13 mmol; our DSC transition data for **1** are: Cr→Col$_h$ 68·4 (39·4), Col$_h$→I 99·5 (6·2); ref. [5 *(a)*] quotes Cr→M 68 (36·3), M→I 97 (3·6)] was achieved in a solvent mixture of diethyl ether and acetic acid for 15 min at RT during which the solution turned green–black. After usual but extremely tedious work-up, including several flash chromatographs (beginning with 800 and moving down to 400 ml silica gel) with elution using l.p./dchm. 3 : 1), a yellow–orange, wax-like product (5·83 g) was obtained. After crystallization from ethanol the final yield of **2** was 5·3 g (47%); $C_{54}H_{83}NO_8$ (874·3). Transition data: Cr→Col$_h$ –/42·9 (12·6), Col$_h$→I 138·0/137·3 (7·4); transition temperatures given in ref. [2], but it is not specified by which method, were Cr→Col$_h$ < RT, Col$_h$→I 136°C. ^{1}H NMR data were identical with those quoted in ref. [2]. With the exception of 8-H and 9-H, the chemical shifts of 4-H, 5-H, and 12-H could now unambiguously be assigned by NOE-studies at 7·90, 7·76, and 7·48 ppm, respectively. ^{13}C NMR, δ_C: 150·47 (1 C), 150·16 (1 C), ~148·9 (3 Cs), as well as 143·79, 140·51, 126·60, 124·64, 124·34, 121·88, 119·28, and 114·29 (each 1 C) = 13 quaternary carbons; 107·78, 107·34, 107·21, 106·84, and 106·43 (5 tertiary carbons); 75·35, 69·88, 69·62, 69·33, 69·24, and 68·72 (6 OCH_2 groups). MS, (210°C), *m/z* 873 (M$^+$, 100; h.r. 873·6119 as calculated for $C_{54}H_{83}NO_8$), 43 (28%); no other signals above 4% intensity.

2.3. *1-Amino-2,3,6,7,10,11-hexahexyloxytriphenylene* [2]

The reduction of **2** (0·875 g, 1 mmol) as described [2] yielded a beige-coloured crude material (0·77 g); after flash chromatography on 100 ml silica gel, eluting with a solvent mixture (l.p./dchm., 1 : 4), and a crystallization from ethanol, 0·41 g (49%) of product was obtained; it was beige in colour and gave needle-like crystals; $C_{54}H_{85}NO_6$ (844·3). Transition data: Cr→Col$_h$ 53·6/54·0 (32·2), Col$_h$→I 69·1/68·3 (2·1); transition temperatures in ref. [2], obtained by an unspecified method were Cr→Col$_h$ 35°C, Col$_h$→I 77°C. ^{1}H NMR data were identical with those quoted in ref. [2]. Here again, cf. the ^{1}H NMR data for **2** given above, with the exception of 8-H and 9-H, the chemical shifts of 4-H, 5-H, and 12-H could be unambiguously assigned by NOE-studies at 7·38, 7·80, and 8·80 ppm, respectively. ^{13}C NMR, δ_C: 150·79, 149·32, 148·72, 147·77, 147·31, 138·36, 135·32; 126·81, 124·58, 124·36, 123·83, 123·78, and 113·78 (13 quaternary carbons); 109·97, 108·25, 107·93, 106·81, and 97·03 (5 tertiary carbons); 73·05 (1 C), 69·80 (2 C), 69·48 (2 C), 69·18 (1 C), and 68·54 (1 C) = 6 OCH_2 groups. MS (250°C), *m/z* 844 (M$^+$, 100%; h.r. 843·6377 as calculated for $C_{54}H_{85}NO_6$), 758 (26%), 130 (20%), 43 (24%); no other signals above 20% intensity.

2.4. *1-Chloro-2,3,6,7,10,11-hexahexyloxytriphenylene* (**3**) [11]

This compound was prepared starting from a stirred mixture of **1** [5 *(a)*] (0·52 g, 0·6 mmol) and aluminium trichloride (100 mg) in 1,2-dichlorobenzene (10 ml) to which sulphuryl chloride (0·07 g, 0·5 mmol, 0·04 ml) was added dropwise; the solution turned dark green–black. This reaction mixture was then stirred for 4 days at RT, before its volatile components were removed *in vacuo,* and the residue was mixed with water, shaken with dchm. (three times), and the extract dried and worked up in the usual way. Finally, the crude product (1·57 g of a dark brown oil) was flash chromatographed several times on 150 ml silica gel, eluting with l.p./dchm. (1 : 1). This gave 180 mg of product which after crystallization from ethanol furnished **3** (170 mg, 32%, greyish–white powder); $C_{54}H_{83}O_6Cl$ (863·7). Transition data: Cr→Col$_h$ –/31·1 (30·8), Col$_h$→95·6/96·1 (4·4); unfortunately, the DSC values in ref. [11] are misprinted and have to be corrected. ^{1}H NMR, δ_H: 9·05 (s; 12-H, assigned by NOE-technique), 7·77 (s, aromatic hydrogen), 7·79 (asymmetric broad signal consisting of three overlapping singlets; 3 aromatic hydrogens), ~4·26–~4·18, and 4·11 (m and t, respectively, $J_t \approx 6{\cdot}5$ Hz; 5 and 1 OCH_2 groups). ^{13}C NMR, δ_C: 151·12, 149·85, 148·85, 148·32, 147·17, 145·59, 127·48, 125·59, 124·71, 124·64, 122·98, 122·84, and 121·68 (13 quaternary carbons); 111·80, 108·21, 107·09, 106·63, and 105·22 (5 tertiary carbons); 73·49, 69·95, 69·70, 69·43, 69·16, and 69·08 (6 OCH_2 groups). MS, *m/z* 863 (M^+, 100%; h.r. 862·5878 as calculated for $C_{54}H_{83}O_6Cl$), 69 (10%), and 57 (12%); no other signals above 10% intensity.

2.5. *1-Bromo-2,3,6,7,10,11-hexahexyloxytriphenylene* (**4**) [11]

Bromine (0·16 g, 1 mmol) was added to a stirred mixture of **1** [5 *(a)]* (0·83 g, 1 mmol) in carbon tetrachloride (5 ml) at ~0°C. After stirring this mixture for four days at RT, dichloromethane was added and a normal work-up carried out. The purification of the brown crude product isolated (1·18 g) was completed by several flash chromatographs, each on 150 ml silica gel, eluting with l.p./dchm. (1 : 1); this yielded a slightly yellowish, wax-like product **4** (0·15 g, ~17%); $C_{54}H_{83}O_6Br$ (908·2). Transition data: $Cr_1 \rightarrow Cr_2$ 30/30·1 (20·6), $Cr_2 \rightarrow Col_h$ 36·9/36·5 (18·8), $Col_h \rightarrow I$ 83·0/83·3 (2·9). ^1H NMR, δ_H: 9·00 (s; 12-H, assigned by NOE-technique), 7·82 (s; aromatic hydrogen), 7·775 asymmetric broad signal consisting of three overlapping singlets; 3 aromatic hydrogens), ~4·28–~4·17, and 4·12 (m and t, respectively, $J_t \approx 6{\cdot}5$ Hz; 5 and 1 OCH_2 groups). ^{13}C NMR, δ_C: 151·08, 149·81, 148·82, 148·38, 146·70, 146·64, 127·75, 124·73, 124·51, 123·28, 123·15, 122·75, and 115·40 (13 quaternary carbons); 111·98, 108·17, 106·97, 106·55, and 105·88 (5 tertiary carbons); 73·35, 69·95, 69·70, 69·40, 69·21, and 69·13 (6 OCH_2 groups). MS, *m/z* 908 (100%), 907 (M^+, ~95%; h.r. 906·5373 as calculated for $C_{54}H_{83}O_6Br$), 745 (~7%), 57 (8%), and 43 (32%); no other signals above 8% intensity.

2.6. *Attempted preparation of the 'mixed, seven-long-tail' 1-hexylthio-2,3,6,7,10,11-hexahexyloxytriphenylene*

Trials on scales between 0·1 and 0·5 mmol of 1-nitro-, 1-chloro-, or 1-bromo-2,3,6,7,10,11-hexahexyloxytriphenylene dissolved in 1,3-dimethyl-2-imidazolidinone (DMEU as an aprotic polar solvent [12] between 2 and 15 ml) were each given times of between 2 and 5 days to react with an excess of sodium hexylthiolate (0·2 or 1 mmol) with stirring at room temperature; the mixtures changed from colourless to orange. The oily or solid crude products obtained after normal work-up were column chromatographed in each case on about 200 ml silica gel (see the general remarks above), eluting with chloroform or mixtures of chloroform and l.p. (2 : 1) or of dchm. and l.p. (1 : 1), but in all three cases none of the desired product could be isolated. Some of the starting materials (**2**, **3**, or **4**, respectively) were recovered, as proved by NMR.

3. Results and discussion

We felt that *mixed* alkoxy and alkylthio or alkylseleno substituted triphenylene would provide another new and large group of disc-like liquid crystal materials with interesting properties. In particular, such mixed derivatives having a single sulphur or selenium bridge between core and chain [6, 13], acting, for instance, as internal [11] electron withdrawing units, should be materials from which one might expect the formation of ordered, wider range, and more stable columnar mesophases like those of the classical [5 *(a)]* triphenylene hexaethers [11].

Key compounds on the route to this goal are the three sevenfold substituted triphenylene derivatives **2**–**4** of which **2** is already known [2]; the two core-halogenated hexaethers **3** and **4** are new and have been prepared for this contribution, although their transition data have already been quoted in another context [11]. Their molecular structures and one-step syntheses are shown in the reaction scheme.

Details of their preparations including the reduction of the 1-nitro compound **2** into the known 1-amino derivative [2], as well as all structural data, are described in §2. The three examples of calculated models of the hypothetical 2,3,6,7,10,11-hexa*methoxy*triphenylene derivatives, in two cases homologues of **2** and **3**, respectively, and shown in figure 1, depict their helically deformed, twisted tetracyclic aromatic cores caused by the crowding of the substituents present in one of the three bay regions. Despite the extremely overcrowded and therefore grossly distorted nature of the 1,12-diiodotriphenylene, synthesized and studied recently [14], we feel it is worth emphasizing that the large bromine could also be introduced into **1** in a normal electrophilic substitution reaction producing the sterically congested, non-planar and chemically stable 1-bromo-hexaether **4**, albeit in only low yield (17%, see §2 and reaction scheme).

The deformed, non-planar aromatic cores give rise to a new case of atropisomerism [15–17], i.e. inducing chirality in **2**–**4** and in any analogous derivative of triphenylene. This unique situation would make further single crystal X-ray information about these molecules very desirable†. Unfortunately, the poor quality of the wax- or powder-like crystals of the low melting compounds **2**–**4**, etc., at present the only available materials in our hands, offer no chance of obtaining such data. Hopefully, a triphenylene hexaether equipped with sub-

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† Molecular mechanics calculations suggested and single crystal X-ray studies of 1,12-di-iodotriphenylene (non-liquid crystalline) proved that its aromatic rings show gross distortions from planarity due to the crowding of the two iodine atoms in the bay region, see ref. [14]. However, the consequences for chirality phenomena were not mentioned there.

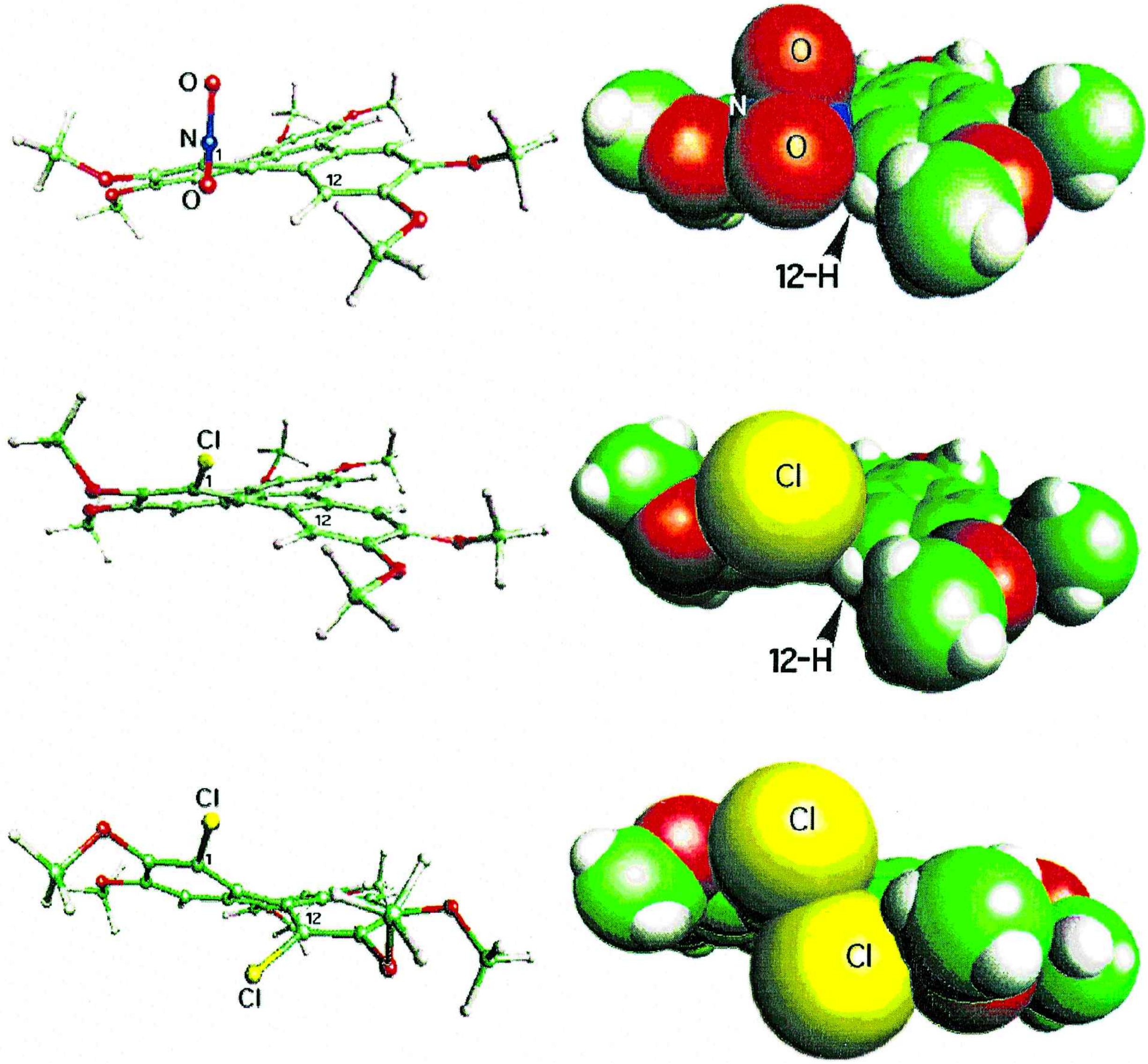
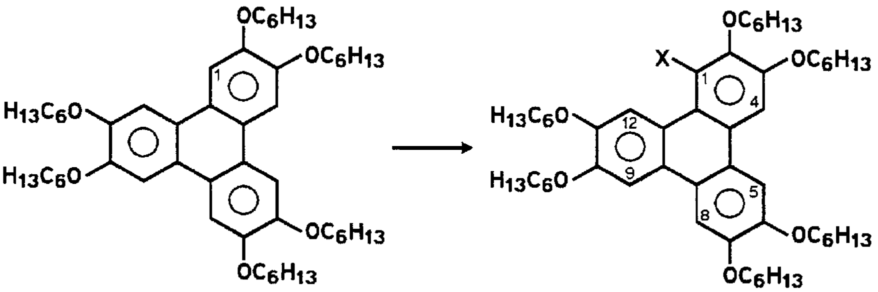


Figure 1. Ball-and-stick as well as space-filling models of the hypothetical 1-nitro-, 1-chloro-, and 1,12-dichloro-hexamethyl-triphenylenes showing the helical deformation/coiled shape of their tetracyclic aromatic cores caused by the substituents at C-1 or C-1 and C-12. The energetically favoured orientation of the NO_2-group is at about 82° with respect to the aromatic core; this situation is shown here. The carbons and hydrogens of the bay region under consideration are numbered: C-1 and C-12 on the left and 12-H on the right. For simplification, the conformational calculations (see § 2.1) were carried out for the *methoxy*-homologues which, however, have not yet been synthesized.

stituents at the α-positions C-1 or C-1 and C-12 and having suitable alkyl chains, i.e. homologues of the hypothetical hexamethoxy derivatives for which our semi-empirically calculated activation energies for their racemization are listed in the table, might solve this problem; relevant synthetic work is in progress. Compared with the range of energy barriers of 67–84 kJ mol^{-1} quoted for the racemization of atropisomers [18], resolution of the racemates of three of the 1,12-dihalogeno-hexaethers recorded in the table, i.e. the 1,12-dichloro-, 1,12-dibromo- or 1,12-diiodo-hexaethers or their alkyl homologues appears possible; for this purpose, detailed chromatographic experiments on suitable enantiomeric stationary phases will be undertaken soon. However, the deviation of their molecular cores from planarity due to the bulkiness of the *two* halogens at the ring positions 1 and 12 might be too large and prevent the formation of thermotropic mesophases by such triphenylene derivatives. Nevertheless, in the event of successful resolution into enantiomers, the determination of their twisting power β would be of interest, as would also be their use as novel chiral dopants.



1 [5a]

2: X = NO_2 [2]
3: X = Cl
4: X = Br

Scheme 1.

Table. Activation energies (E_a) for the racemization obtained by semi-empirical calculations (see § 2.1) for eleven *hypothetical* derivatives of the disc-like parent model compound 2,3,6,7,10,11-hexamethoxytriphenylene [5 (*a*)] each carrying one or two of the substituents (selected and listed in the left and right part of the table) at the assigned carbon atoms of the triphenylene core, causing gross distortions of the aromatic rings from planarity (thereby introducing helical chirality!) due to the crowding of the substituents in one of the three molecular bay regions (see the three selected models in figure 1). For economy in computing time, all calculations were carried out for the respective hexa*methoxy* homologues.

Substituent[a]	E_a/kJ mol^{-1}	E_a/kJ mol^{-1}	Substituents[a]
1-CH_3	47·8	—	—
1-CN	19·3	—	—
1-NH_2	24·1	—	—
1-F	2·9	21·3	1,12-di-F
1-Cl	15·7	179·4	1,12-di-Cl
1-Br	22·2	224·5[b]	1,12-di-Br
1-I	26·8	203·1[b]	1,12-di-I

[a] Selective functionalization at carbon atom C-1 or carbon atoms C-1 and C-12, e.g. 1,12-di-I = 1,12-diiodo-2,3,6,7,10,11-hexaalkoxytriphenylene.

[b] Since these energies of activation are relatively close to those of dissociation of the respective halogen–carbon bonds and the distances between the halogens are quite short, reactions other than racemization might also take place at elevated temperatures. Nevertheless, our calculations show that under ambient conditions the enantiomers do not racemize.

Regarding the NMR data for the two new, overcrowded sevenfold substituted triphenylene mesogens **3** and **4**, with chlorine or bromine instead of an alkoxy group in the α-region, at C-1, it is noted that the 12-H hydrogens 'opposite' and hidden in a bay (see figure 1) suffer a similar strong downfield shift: their average δ_H-value is 9·03 compared with 9·12 on average over six 1-alkoxy/-methoxy cases [3]. In this series of core-twisted compounds, an amino group at C-1 shifts the 12-H hydrogen less downfield, only to $\delta_H = 8{\cdot}80$. Interestingly, a methyl group having, as said [19], 'effectively the same size as a chlorine substituent' (however, cf. our calculation results of the table) and used in place of X, at C-1, causes a still weaker downfield shift ($\delta = 7{\cdot}90$! [20]) of the 12-H hydrogens. In our opinion, these resonance data for both 12-H hydrogens in **1** with chlorine or a methyl group at C-1 clearly demonstrate that steric factors [3] are not alone responsible for the big shift difference ($\Delta\delta_{12\text{-}H} = 1{\cdot}15$ ppm!); electronic effects must be involved to a high degree.

These considerations are also relevant whether thermomesomorphism occurs for the 2,3,6,7,10,11-hexahexyloxytriphenylene derivatives with X = Cl (**3**) or CH_3 [21] (cf. the reaction scheme and figure 2). Compound **3** is a disc-like mesogen which, due to the powerful internal [11, 22] electron-acceptor function (Cl), possesses enhanced columnar [10] phase properties compared with the parent compound **1**. The 1-methyl derivative [21] is *not* however mesomorphic which, here, is solely attributable to the sterically overloaded situation. Similar suppressions of columnar phases caused simply by a methyl group are already known, for example from the field of inositol liquid crystals; hexaesters of mytilitol [23]—a naturally occurring aliphatic hexol [24] carrying one methyl group perpendicular to its cyclohexane ring (in the chair conformation)—are *non*-thermomesomorphic [23], whereas the same hexaesters of another inositol without the perturbing methyl group, i.e. of scyllitol, *do* exhibit a columnar type of phase [25]. Not only methyl but also, e.g. hydroxyl or alkoxy groups in sterically unfavourable, axial positions of saturated cyclic sytems can act in the same way [26–29].

In this connection it may be of interest to add that the mesogenicity of calamitic compounds is also negatively affected by methyl groups located in sterically burdened positions [23, 30], but to a much lesser extent.

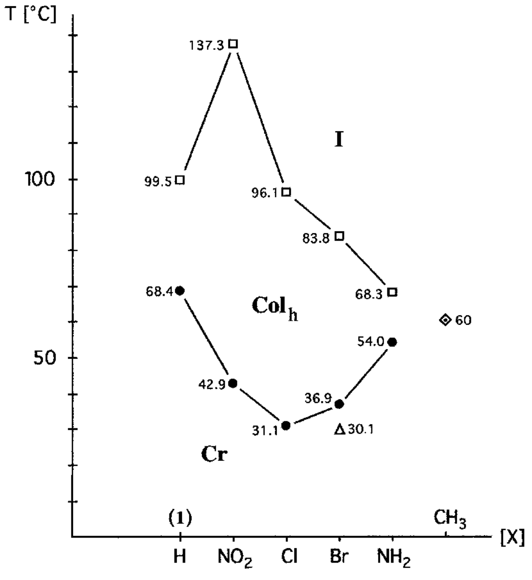


Figure 2. Plot of the phase transition temperatures of the triphenylene hexahexyl ether (1) and five derivatives differently X-substituted at carbon atom C-1 (see §2 and reaction scheme; see also footnote †) determined by DSC in our laboratory; ● melting and □ clearing points, △ crystalline–crystalline transition point, ◇ m.p. of the non-thermomesomorphic methyl analogue ($X = CH_3$) quoted from ref. [21]. The given assignment Col$_h$ [10] for the mesophase region applies for all five liquid crystalline hexaethers and the properties of the phase tally with other authors' descriptions [2, 3]. The temperature ranges of the five mesophases are f.l.t.r. 31·1, 94·4, 65·0, 46·9, or 14·3 K.

However, disc-like materials with a distinct mode of columnar arrangement in their mesophases, understandably respond much more sensitively to steric perturbations at the upper or lower surfaces of their cores, presumably through blocking of the sites at which the spontaneous face-to-face stackings take place.

The transition temperatures of the parent hexaether **1** and of the five of its 1-substituted derivatives obtained (with the exception of the 1-methyl compound [21]) by DSC in our laboratory are depicted graphically in figure 2 allowing one to see at a glance the different electronic influence of the substituents at carbon atom C-1 of **1** (cf. reaction scheme), on the temperature range (between 14·3 and 94·4 K) and thermal stability of the columnar phases of these electron-rich disc-like compounds. Three of them, **2**–**4** (with the nitro-, chloro-, or bromo-substituent) and also the 1-fluoro-analogue†, including the same compounds **3** and **4** independently synthesized by British colleagues [17], can be seen as mesogens which have incorporated single substituents with donor or acceptor functions giving heavily substituted, non-planar molecules [11] and *enhancing* the mesophase properties due to π-π interactions in such unique dipolar situations. A drastic narrowing of this mesophase range occurs with the 1-amino (donor)substituted hexaether and the phase disappears completely in the case of the 1-methyl analogue (see discussion above).

All five mesophases of figure 2 are fully miscible among themselves and are of the columnar hexagonal type as described earlier [2, 3] for **1**, **2**, and the *N*-acyl derivatives of 1-aminotriphenylene hexaether.

A surprising exception in this series of mesogens is the 1-bromo derivative **4** which shows, in addition to the two phase transitions common to most of the members, a crystalline–crystalline transition (see figure 2 and §2). Both transitions lying below the liquid crystalline state can be strongly supercooled.

Finally, however, we are forced to acknowledge that all our attempts to substitute the three different acceptor substituents in **2**–**4** by a hexylthio group failed, i.e. our goal to synthesize for the first time disc-like, triphenylene based thermotropic liquid crystal materials with *seven* longer alkyl chains bridged to the tetracyclic aromatic core by *two* types of chalcogens could not be reached.

We thank Professor N. Boden, Dr R. J. Bushby, Dr A. N. Cammidge, and their coworker, G. Headdock, B.Sc., School of Chemistry and Centre for Self-Organizing Molecular Systems, University of Leeds, U.K., for their kind co-operation and prior communication (9 September 1996) of a paper [17] submitted on core-twisted disc-like triphenylene-based mesogens. We also thank Privatdozent Dr J. Jakupovic in our Institute for his assistance in carrying out NOE experiments and the Rechenzentrum (ZRZ, project 6227), of the University for computer services. Financial support by the Deutsche Forschungsgemeinschaft (Sfb 335, 'Anisotrope Fluide', project C3), the Fonds der Chemischen Industrie, the Technische Universität Berlin, and the Gesellschaft von Freunden der Technischen Universität Berlin is gratefully acknowledged.

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†Note added in October 1996. Our DSC measurements on 1-fluoro-2,3,6,7,10,11-hexahexyloxytriphenylene [17]—a colourless sample gratefully received from Dr R. J. Bushby, University of Leeds, U.K. on 30 September 1996—furnished the following phase transition data: Cr→Col$_h$ 43·4°C (ΔH 39·8 kJ mol^{-1}), Col$_h$→I 123·9°C (ΔH 8·3 kJ mol^{-1}), mesophase range 80·5 K.

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