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The Influence of Lateral Apolar Substituents on the Mesomorphic Behaviour of Tetracatenar Liquid Crystals

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Abstract—Several series of new tetracatenar mesogens consisting of a five-ring aromatic core and bearing one or more apolar lateral substituents in the central benzene ring of the molecule have been synthesized and their mesomorphism is characterized by polarization microscopy, differential scanning calorimetry, and X-ray diffraction methods. Introduction of one, two, or four methyl groups into these tetracatenar mesogens destabilized columnar organization typical of the long-chain homologs, but did not suppress smectic C and nematic phases. Introduction of larger substituents did, however, suppress lamellar organization ($C_{15}H_{31}$) or mesomorphism (*tert*-butyl) totally.

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Polycatenar liquid crystals are a class of thermotropic mesogens composed of rigid elongated core and at least three terminal flexible aliphatic chains (Fig. 1), and they are generally classified as hexacatenar, pentacatenar, tetracatenar, etc., depending on the total number of alkyl chains attached [1]. Perhaps the most remarkable thing about polycatenar mesogens is that at one extreme (tricatenar mesogens) they show the mesomorphism typical of calamitic materials, while at the other (hexacatenar mesogens) they show columnar mesophases, commonly found in discotic materials [1, 2]. The appearance of certain phase depends on the relative proportion of aliphatic and non-aliphatic regions in the molecular structure, which is best illustrated by certain tetracatenar mesogens that can exhibit the whole range of mesomorphic organization i.e nematic, smectic, cubic and columnar phases [3]. The reasons for columnar organization in these materials are not apparent immediately, but models exist explaining this behavior and showing that the columns consist of groups of molecules [4, 5]. In general then, the phase shown by a polycatenar mesogen depends on the balance between the cross-sectional area of the molecular core and the cross-sectional area of the chains projected onto the core-chain interface, which increases as the number or length of the attached chains increases.

The mesomorphism of diskotic mesogens also depends on the degree of coverage of the periphery by flexible chains, and this idea was exploited by Praefcke et al. [6] when they studied the lyotropic liquid crystal properties of a series of giant disks containing palladium and platinum. Here they used organic solvents to modify the mesomorphism and they introduced an idea of “internal” and “external” solvent, where internal solvent represents the alkyl

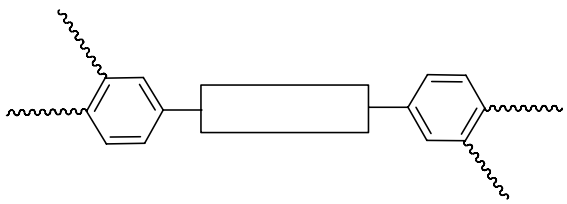
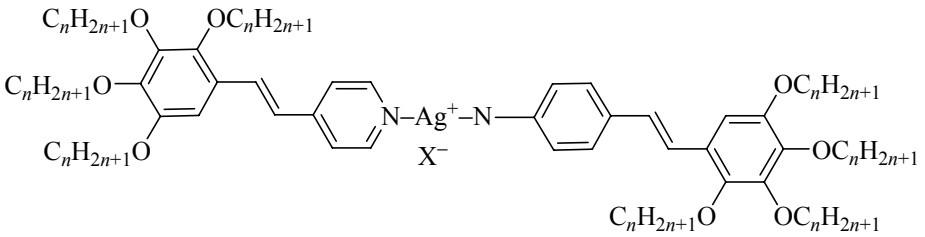


Fig. 1. Schematic representation of a tetracatenar mesogen.

chains attached covalently to the discotic core, while external solvent was the added hydrocarbon used to induce lyotropic phases.

With these results in mind, we undertook a study of the lyotropic liquid crystal behaviour of some polycatenar complexes of silver **I**.



I

It was the first study of lyomesomorphism in polycatenar systems [7, 8]. It was shown in this study that added polar solvents tended to associate with polar core of the complexes **I**, while non-polar solvents associated with non-polar periphery. For example, if the material showed a cubic phase, then a columnar phase could be induced by adding alkane solvent to the system, as the alkane associates with the terminal chains and not the core, effectively increasing the volume of the former. Conversely, when a molecule shows a columnar phase, the addition of polar solvents causes an effective increase in the volume of the central part of the molecule, which is equivalent to reducing the volume of the periphery. As a consequence, a cubic phase is induced. Moreover, we discovered chromonic behaviour [9] using small polar protic solvents (short-chain alcohols). In these systems the solvent caused the complexes to form through hydrogen bond the ribbon-like structures and so nematic, tetragonal and lamellar phases were obtained [7, 8].

Table 1. Mesomorphism of 3,4-dialkoxybenzoyloxybenzoic acids

Compound	Phase transition	*T*, °C
A-10	Cr–Cr'	123.3
	Cr'–I	153.5
A-12	Cr–Cr'	105.8
	Cr'–I	143.8
	I–(N)	142.5
A-14	Cr–Cr'	105.8
	Cr'–SmC	136.7
	SmC–I	139.0
A-16	Cr–Cr'	113.1
	Cr'–Col	131.3
	Col–I	135.0
A-18	Cr–Cr'	118.5
	Cr'–Col	127.6
	Col–I	132.1

However, complexes **I** differ from the more typical polycatenar materials in a number of ways. For example, they contain a metal, they have a charge in the centre, they have a bulky anion associated with that cation, and they are unique as materials that are mesomorphic with six peripheral chains with only four aromatic rings in the core. It was therefore of considerable interest to prepare a series of more conventional polycatenar mesogens and to examine their behaviour as potential lyotropic mesogens.

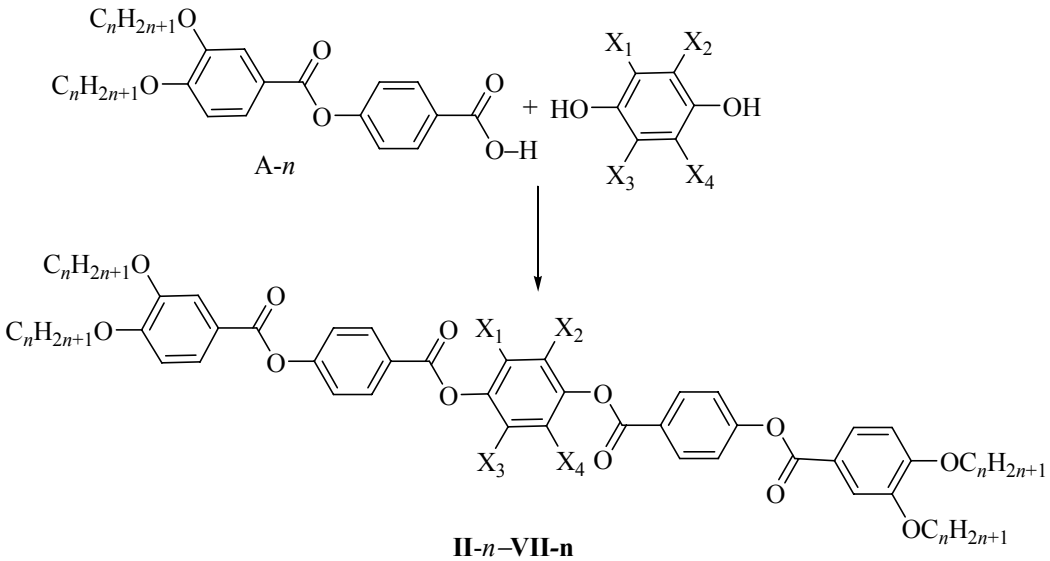
The compounds studied have an aromatic core composed of five benzene rings connected by ester groups all of which are oriented towards the centre of the molecule; the terminal chains are located in the 3,4-positions and provide more dense molecular packing. Introduction of lateral, apolar substituents into the middle part of the molecule allowed the molecular structure to be varied with the aim of decreasing both the melting and clearing points of the mesogens.

Another aspect of lateral substitution (especially the substitution with the long aliphatic chain like in compound, **VI**) is that it is analogous to the alkylsulfate anion of compounds **I**. Thus, in the case of these polycatenar silver complexes, the long-chain anion contributed partly to the terminal chain volume at certain lengths when it was able to extend past the end of the rigid core of the complex [10].

The compounds investigated in this work were synthesized according to Scheme 1.

Thus, 3,4-dialkoxybenzoyloxybenzoic acids [11] were esterified with the appropriate 1,4-hydroquinone using DCC/DMAP in dichloromethane at room

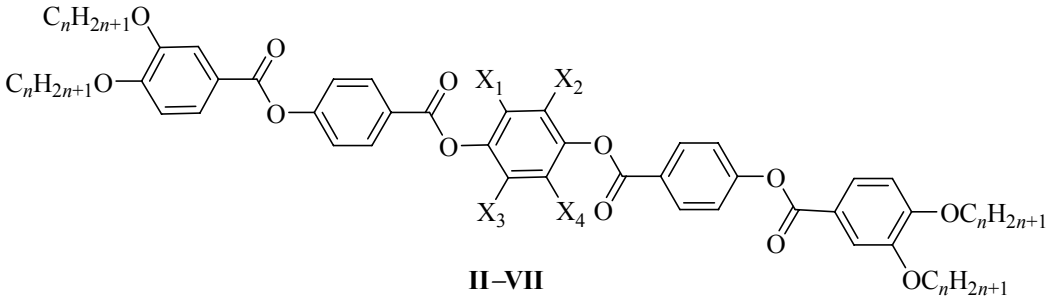
Scheme 1.



temperature. Most of the hydroquinones were available commercially, but those required for compounds **V** and **VI** were prepared by published methods (see Experimental). The ^{1}H NMR spectra of the products showed a typical AMX spin system for the ring bearing the dialkoxy fragments and an AA'XX' system for the next ring towards the centre. The splitting pattern for the central ring depended on the hydroquinone used in the reaction. Yields, NMR spectra, and analytical data are collected in the Experimental.

Mesomorphism. Data on mesomorphic properties of acids shown in Table 1 differ markedly from those reported in [11]. Thus, the shortest-chain homologue A-10 we obtained is non-mesomorphic (in agreement with [11]), while the rest of the materials exhibit the mesomorphism. Thus, for n = 12, we find a monotropic nematic phase (Tuffin et al. [11] report the same behaviour with almost identical temperatures for the C14 homolog), while for A-14 we see an enantiotropic SmC phase. For both A-16 and A-18, we observed an enantiotropic columnar phase, although we did not assign its symmetry. We note that in [11] A-16 is reported as having both a monotropic nematic and columnar hexagonal phase, while in A-18 [11] reports a monotropic Col_h phase. In both cases we agree on the temperature of transition to isotropic. However it is doubtful that a nematic phase appears in a tetracatenar mesogen of this type with C16 chains (Scheme 2).

Scheme 2.



II-*n*, $X_1 = X_2 = X_3 = X_4 = H$; **III**-*n*, $X_1 = X_3 = X_4 = H$, $X_2 = Me$; **IV**-*n*, $X_1 = X_2 = Me$, $X_3 = X_4 = H$; **V**-*n*, $X_1 = X_2 = X_3 = X_4 = Me$; **VI**-*n*, $X_1 = X_3 = X_4 = H$, $X_2 = C_{15}H_{31}$; **VII**-*n*, $X_1 = X_3 = H$, $X_2 = X_4 = t$-Bu.

Table 2. Differential scanning calorimetry data for compounds **II–VII**

Compound	Phase transition	T, °C	ΔH, kJ mol^{-1}	ΔS, R
II-10	Cr–SmC	153.6	69.2	162
	SmC–N	174.4	9.7	22
	N–I	183.3	1.1	2
II-12	Cr–SmC	162.5	73.7	169
	SmC–N	170.2	4.7	11
	N–I	171.9	0.7	2
II-14	Cr–Col_r	154.0	72.2	169
	Col_r–SmC	162.7	0.6	1
	SmC–I	164.3	8.2	19
II-16	Cr–Col_r	145.8	71.2	170
	Col_r–I	158.9	9.0	21
III-10	Cr–SmC	127.7	9.6	24
	SmC–N	148.1	86.2	205
	N–I	162.0	1.2	3
III-12	Cr–Cr'	127.5	16.4	41
	Cr'–SmC	133.6	68.4	168
	SmC–N	143.9	9.4	23
	N–I	151.5	1.3	3
III-14	Cr–SmC	130.7	111.2	275
	SmC–N	142.2	7.1	17
	N–I	144.7	0.6	1
III-16	Cr–SmC	130.4	123.7	307
	SmC–I	137.2	8.6	21
III-18	Cr–(SmC)	126.3	142.3	356
	(SmC)–I	132.5	7.9	20
IV-10	Cr–SmC	134.8	81.9	201
	SmC–N	163.0	11.8	27
	N–I	176.4	1.3	3
IV-12	Cr–SmC	133.0	99.3	245
	SmC–N	157.1	10.6	25
	N–I	163.4	1.2	3
IV-14	Cr–SmC	133.5	115.5	284
	SmC–N	155.7	5.9	14
	N–I	157.2	0.6	1
VI-12	Cr–N	102.9	52.7	140
	N–I	107.7	1.5	4
VII-10	Cr–I	125.1	99.8	251
VII-12	Cr–I	120.4	107.0	272
VII-14	Cr–I	120.0	124.7	317

The polycatenar mesogens **II** to **VII** were studied by polarization optical microscopy and DSC to determine their mesomorphism. Results of these experiments are compiled in Table 2.

Parent laterally unsubstituted compounds **II**-*n* showed the expected and classical succession in mesomorphism with the increasing chain length. Thus for both n = 10 and 12 a SmC and a nematic phases were seen which were identified readily from their characteristic optical textures. As the chain length increased to n = 14, the nematic phase disappeared and a columnar phase was seen beneath the SmC phase; the latter was now much reduced in range, appearing at 162.7°C and clearing at 164.3°C. As the chain length increased further to n = 16, the lamellar phase disappeared totally and the only phase observed was the columnar phase. A noticeable feature of the behaviour is the reducing stability of the clearing point of the materials with the increasing chain length, although the crystal phase stability does not follow the same pattern. Interestingly, the mesomorphism of these compounds is effectively the same as in the related materials (**VIII**-*n*) reported by Nguyen et al. [12] except for the mesomorphic ranges in homologues with the longer chains **VIII**-12 and **VIII**-14 being a little wider owing to a less stable crystal phase. The explanation for this trend in mesomorphism with increasing chain length is very well documented and discussed elsewhere [4, 13] (Scheme 3).

As suggested earlier, in considering undertaking lyotropic studies of these polycatenar materials, there

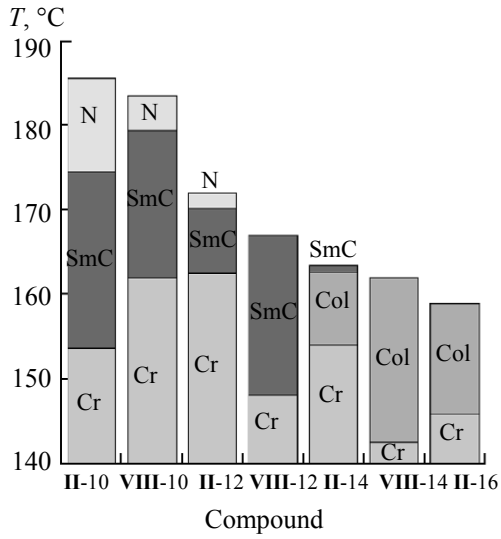
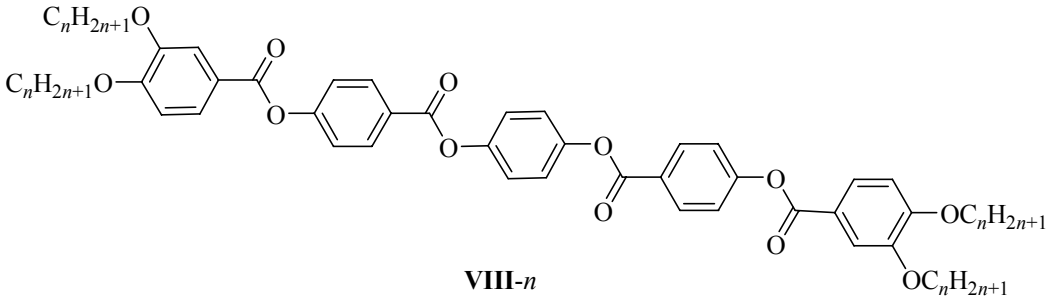


Fig. 2. Comparison of the mesomorphism of compounds **II**-*n* and **VIII**-*n* (no data available for **VIII**-16).

Scheme 3.



VIII-*n*

was a concern that the transition temperatures may be rather high and so the introduction of lateral substituents was considered as a profitable way in which they might be modulated. The first series of materials examined (**III**-*n*) possessed a lateral methyl group and five homologs were prepared. Introduction of this lateral methyl group was found to destabilize the crystal phase on the average between 10 and 20°C and to reduce clearing points by some 20°C. However, there was also a profound effect on the mesomorphism as the columnar phase was now totally suppressed. The phase diagram (Fig. 3) shows a steady decrease in clearing point with small variations in melting point, but compared to compounds **II**-*n*, the nematic phase persists to $n = 14$, while the SmC phase is seen across all homologs prepared, although its stability falls off rapidly at $n = 18$.

In moving to compounds **IV**-*n*, a second methyl group is added to the hydroquinone ring and, curiously, the thermal stability of the mesophases increased compared to those found for **III**-*n*, although there was little effect on the melting point; this is illustrated in Fig. 4. Thus, for **IV**-12 and **IV**-14, the SmC range is much greater, almost double, while for **III**-10 and **IV**-10 the range is about the same on account of the lower stability of the crystal phase in the former compound. Nematic ranges do not appear to vary very much. One possible explanation for this is that compounds **IV**-*n* have a higher symmetry than **III**-*n* and it is well known that lower symmetry reduces packing efficiency, and thus this may be the reason for the decrease. Then, if compounds **II**-*n* and **IV**-*n*, are compared, the latter possessing two methyl groups, both with high molecular symmetry, then the steric effect can be discerned by comparison between their thermal behaviour; in compounds **IV**-*n* a considerable destabilization of the crystal phase is observed and less essential destabilization of the clearing points (Table 2).

Only one homolog, **V**-12, was prepared using the tetramethylhydroquinone core as it was found that the

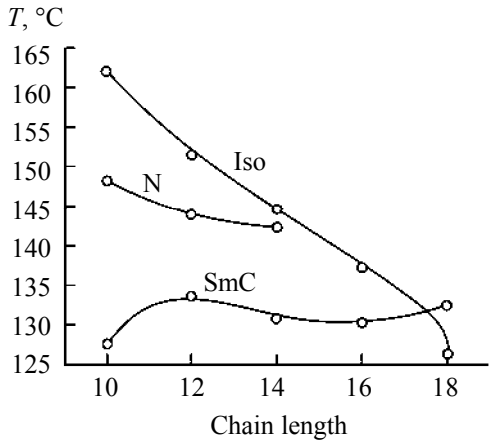


Fig. 3. Mesomorphism of compounds **III**-*n*.

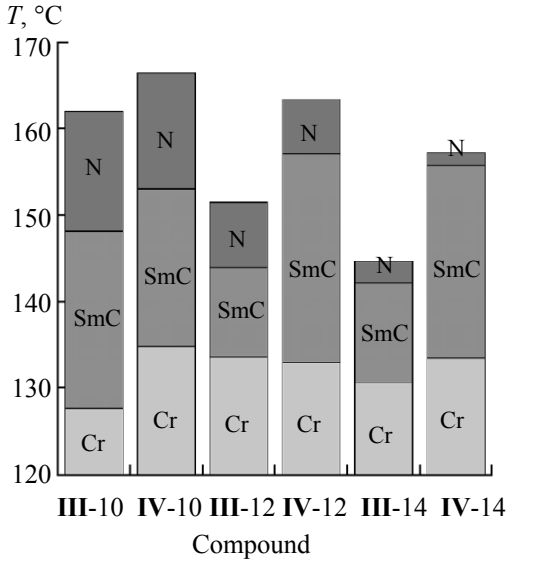


Fig. 4. Comparison of the mesomorphism of compounds **III**-*n* and **IV**-*n*.

Table 3. X-ray data of compounds **II**-14 and **II**-16

Compound	*T*, °C	Experimental reflexes d_{exp},[a] Å	Intensity	*hkl*	Cell parameters	*hkl*	Cell parameters
II-14	158	36.52	v.s[b] (sh)	11	*a* 65.8 Å[c]	20	*a* 73.04 Å
		32.9	s (sh)	20	*b* 43.9 Å[c]	11	*b* 36.85 Å
		4.6	v.s (w)		*S* 1444 Å^2		*S* 1346 Å^2
	160	36.42	v.s (sh)	11	*a* 65.48 Å	20	*a* 72.84 Å
		32.74	s (sh)	20	*b* 43.82 Å	11	*b* 36.65 Å
		4.6	v.s (w)		*S* 1435 Å^2		*S* 1335 Å^2
	166	36.52	v.s (sh)	001	*d* 36.52 Å[d]		
		4.6	v.s (w)		*A* 64 Å^2		
II-16	150	38.13	V.s (sh)	11	*a* 68.16 Å	20	*a* 76.26 Å
		34.08	s (w)	20	*b* 46.0 Å	11	*b* 38.1 Å
		4.6	v.s (w)		*S* 1568 Å^2		*S* 1453 Å^2
	155	37.75	v.s (sh)	11	*a* 67.3 Å	20	*a* 75.5 Å
		33.65	s (sh)	20	*b* 45.6 Å	11	*b* 37.6 Å
		4.6	v.s (w		*S* 1534 Å^2		*S* 1419 Å^2

[a] d_{exp} are experimental reflexes, *hkl* are Miller indexes. [b] (v.s) very strong, (s) strong, (sh) sharpe, (w) wide. [c] *a*, *b* are cell parameters for Col_r phase, *S* is column square. [d] *d* is layer distantion for SmC phase, *A* is molecular square in SmC phase.

compound was subject to thermal decomposition as soon as the isotropic state was reached. Thus, from one heating cycle, the following transition sequence was found: Cr·108–109·SmC·130.5·Iso.

For compounds **VI**-*n*, again only one homolog was prepared, namely **VI**-12. This compound was designed as a covalent analog of the silver(I) stilbazole complexes that we had studied earlier and which possessed a lateral dodecylsulfate anion, whose chain length equates to fifteen atoms when the O–S–O link of the sulfate group is taken into account. Previously we used a similar approach in preparing neutral platinum(II) analogues of these silver complexes [15]. In this case, only a nematic phase was seen with a rather narrow range and both the crystal state and the mesophase had been significantly destabilized.

Finally, three homolog of **VII**-*n* were prepared (*n* = 10, 12 and 14), but the steric effect of the *tret*-Bu group was simply too great and none of the compounds was mesomorphic, all melting close to 120°C.

X-ray investigation. Inasmuch as the symmetry of columnar phases is notoriously difficult to determine from optical textures alone, compounds **II**-14 and **II**-16 were further investigated by X-ray diffraction (Table 3). For **II**-14, the X-ray data are consistent with the assignment of the higher-temperature phase as lamellar, and a (001) reflection is observed corresponding to a layer spacing of 36.52 Å which, given a molecular length (all *trans* conformation) of 68.4 Å and assuming no interdigitation, would correspond to a tilt angle of 58°. The expected reflection corresponding to the flexible alkyl chains was also observed at 4.6 Å. The X-ray data showed that the molecular area in the SmC phase was about 64 Å^2, i.e. 32 Å^2 for a single chain, which is reasonable for a SmC phase [16].

The columnar nature of the lower-temperature phase was confirmed by X-ray analysis, and two reflections corresponding to the fundamental reflections of a rectangular lattice were observed. The two reflections proved insufficient to identify the plane group unequivocally and so it is not possible to assign the plane group to one of the two most likely possibilities, namely *c2mm* or *p2gg*. This also means that unequivocal assignment of the two, lowest-angle peaks as (11) and (20) is not possible and so Table 3 shows the lattice parameters calculated for both possibilities. Homolog **II**-16 shows only a columnar mesophase, which is also rectangular and again, the plane group cannot be determined. The possibilities are the same as for **II**-14 and the lattice parameters are comparable when the increased terminal chain length is taken into account.

Lyotropic mesomorphism. No solvent-induced behaviour was observed for any of the above

compounds in contact preparations with apolar (alkanes of different length) or polar (DMSO, DMF) solvents and the materials simply dissolved in the solvents used at a given temperature. Given the results obtained previously with inositols [17], palladium discs [6] and polycatenar silver(I) complexes [7, 8], this is perhaps surprising and the question will be tested further with the preparation of additional materials.

The literature contains only few examples of laterally substituted polycatenar mesogens, but two examples are shown as **IX** and **X** along with their mesomorphism [1, 2] (Scheme 4).

Thus, **IX** has a monotropic SmC phase while **X** shows a monotropic N phase. It is well known in calamitic systems that lateral alkyl groups suppress lamellar phases in favor of the nematic phase [18], but in **III**-*n* and **IV**-*n*, and in **IX** and **X**, it is the columnar phase that is suppressed while the SmC phase persists.

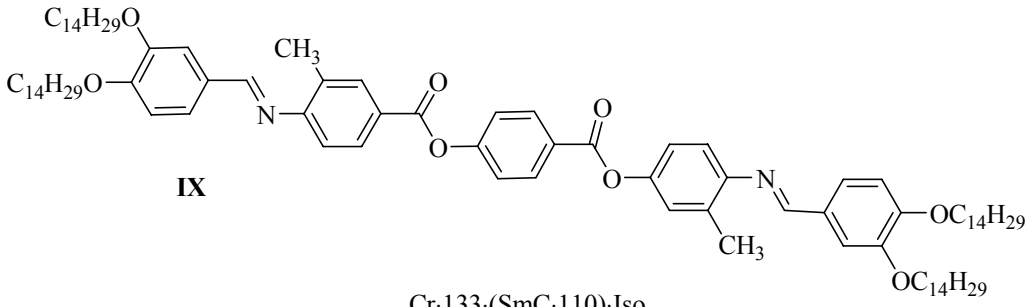
Lateral substitution, therefore, has an effect that is different in polycatenar systems when compared to conventional calamitics. Thus, in calamitic materials, the reason for the suppression of lamellar phases is obvious as the lateral group prevents the molecules associating into layers. However, it is important to note that such arguments apply only to substituents with a size from about methyl group and larger, for it is well known that lateral fluorination is a productive strategy for controlling both smectic and nematic mesomorphism in calamitic systems [19]. As stated earlier, in polycatenar systems, the SmC is the only smectic phase observed and the formation of the tilted phase is driven by the mismatch in cross-sectional area of the molecular core and cross-sectional area of the chains projected onto the core-chain interface. To some extent then, lateral groups are more shielded sterically and so can be accommodated within the tilted phase with disrupting it. If this is true, it is then a little more difficult to rationalise the suppression of columnar phases, when the columnar phase is still not evident even when n = 18 (**III**-18: SmC) and when the lateral bulk is doubled (**IV**-*n*) and the lamellar phase stability increases. Nonetheless, the models discussed by us and others do require that the SmC phase breaks up into small separate columns that organize to form the column and, superficially at least, it is unsurprising that the lateral groups appear to inhibit this process. However, the forgoing discussion emphasises the fact that the explanation is not quite so straightforward.

EXPERIMENTAL

Polarization optical microscopy was performed on microscope Leitz Laborlux 12 Pol fitted with Mettler heating block FP90.

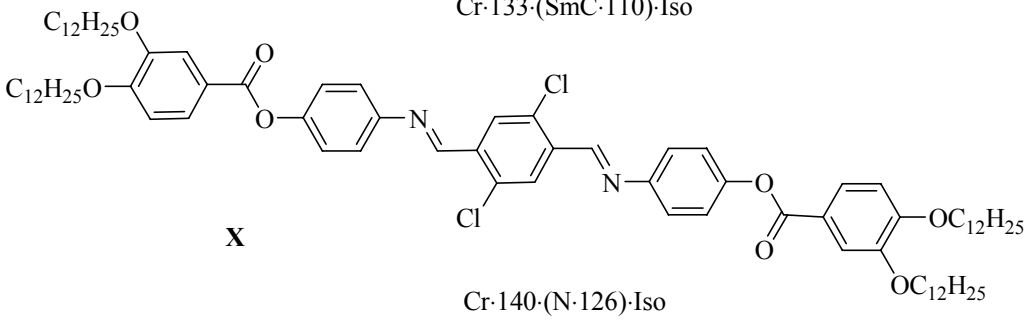
Differential scanning calorimetry was carried out at a rate 10 K min^{-1} on Mettler DSC822^e (running on the Star^e software which is equipped with an auto-

Scheme 4.



IX

Cr·133·(SmC·110)·Iso



X

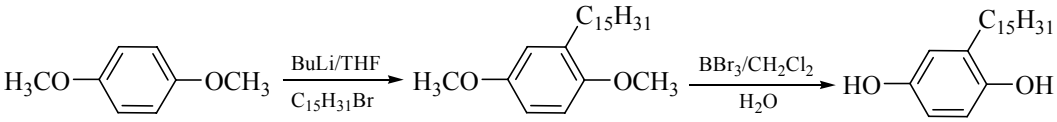
Cr·140·(N·126)·Iso

sampler). DSC data mentioned in this article are onset temperatures.

The X-ray patterns were obtained with two different experimental setups, and in all cases, the powdered sample was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. A linear monochromatic CuK_a beam (λ = 1.5405 Å) obtained with a sealed-tube generator (900 W) and a bent quartz monochromator were used (both generator and monochromator were manufactured by Inel). One set of diffraction patterns was registered with a curved counter Inel CPS 120, for which the sample temperature is controlled within ±0.05°C from 20 to 200°C; periodicities up to 60 Å can be measured. The other set of diffraction patterns was registered on Image Plate. Periodicities up to 90 Å can be measured, and the sample temperature is controlled within ±0.3°C from 20 to 350°C.

Compounds were characterized by ^{1}H NMR spectroscopy using a Jeol JNM-EX 270 FT NMR system at 270 MHz for ^{1}H NMR and 68 MHz for ^{13}C NMR, while elemental analysis was carried out at the University of Newcastle.

2-Pentadecyl-1,4-hydroquinone [20].



n-Buthyl lithium (2.5 M, 34 ml, 86 mmol), was added to a solution of 1,4-dimethoxybenzene (11.8 g, 85 mmol) in THF (20 ml) in a 500-ml two-neck round-bottom flask at 0°C. The solution was stirred for 1 h and then transferred dropwise into a solution of bromopentadecane (29.9 g, 103 mmol) in THF (20 ml) in another round-bottom flask. The resulting mixture was stirred at room temperature for **I** h and then poured into water (100 ml). The mixture was extracted with diethyl ether (3×30 ml); the organic layers were combined, washed with brine (30 ml), and dried over magnesium sulfate. After removal of solvent, the crude product was subjected to column chromatography on silica gel (60 μm) with dichloromethane as eluent. The resulting product is a colourless liquid. Yield: 14.1 g, 47% . ^{1}H NMR (270 MHz, $CDCl_3$): 6.72–6.67 m (3H, ArH), 3.75 s (3H, CH_3O–), 3.74 s (3H, CH_3O–), 2.57–2.52 t (2H, –CH_2–), 1.86–1.80 m (2H, –CH_2–), 1.5–1.2 m (24H, –$C_{12}H_{24}$–), 0.88–0.83 t (3H, –CH_3)

Table 4. Elemental analysis data for compounds **II–VII**

Compound	Yield, %	Calculated (Found), %	
		C	H
II-10	65	75.09 (75.29)	8.69 (9.07)
II-12	72	76.01 (76.32)	9.18 (9.20)
II-14	25	76.77 (76.98)	9.59 (9.56)
II-16	3	77.43 (77.54)	9.95 (9.94)
III-10	45	75.22(75.22)	8.85 (8.80)
III-12	30	76.11 (76.26)	9.23 (9.40)
III-14	16	76.86 (77.02)	9.64 (9.80)
III-16	6	77.50 (77.24)	9.99 (10.40)
III-18	3	78.05 (77.42)	10.28 (11.48)
IV-10	36	75.34 (75.19)	8.82 (8.87)
IV-12	43	76.21 (76.18)	9.29 (9.31)
IV-14	28	76.95 (76.70)	9.69 (9.78)
VI-12	85	77.35 (77.31)	9.90 (9.91)
VII-10	44	76.01 (76.34)	9.18 (9.20)
VII-12	61	76.77 (76.74)	9.59 (9.97)
VII-14	65	76.43 (77.16)	9.95 (10.43)

The compound so obtained (7.05 g) was dissolved in dichloromethane (50 ml) and added slowly to a solution of BBr_3 (10.01 g, 0.041 mol) in dichloromethane (10 ml) at –78°C. After the addition was complete, the solution was warmed up slowly to room temperature and stirred for 24 h. The solution was then added to an ice-water mixture with vigorous stirring and the precipitated product was filtered off, washed with water (25 ml), and dried. The product was separated by column chromatography on silica gel (60 μm) using hexane/ethyl acetate mixture (2:1) as the eluent. Yield 3.4 g (53%). ^{1}H NMR spectrum (270 MHz, $CDCl_3$): 6.51–6.45 m (3H, ArH), 2.4–2.3 t (2H, –CH_2–), 1.42–1.39 m (2H, –CH_2–), 1.15–1.11 m (24H, –$C_{12}H_{24}$–), 0.75–0.71 t (3H, –CH_3,)

Tetrametylhydroquinone was obtained by reduction of the corresponding quinone with *N,N*-diethylhydroxylamine following the procedure described in [21].

General procedure for the synthesis of tetracatenar compounds ***II–VII***. The appropriate 4-(3,4-dialkoxybenzoyloxy)benzoic acid (0.0015 mmol), the required phenol (8×10^{-4} mmol), dicyclohexylcarbodimide (DCC, 0.002 mmol), and 4-dimetylaminopyridine (~40 mg) were stirred in dry dichloromethane (50 ml) under a nitrogen atmosphere for 24 h. The resulting mixtures were purified by flash column chromatography over silica gel (60 μm), using dichloromethane as the eluent. For the synthesis of the longer-chain homologs, up to five times more solvent was used than for the lower homologs, and the reaction was allowed to proceed at 36°C for 3 days. The elemental analysis data of compounds obtained are given in Table 4.

II-*n*: ^{1}H NMR spectrum (270 MHz; $CDCl_3$): 8.3 m (4H); 7.8 d.d (2H); 7.7 d (2H); 7.37–7.34 m (4H); 7.3 s (4H); 6.9 d (2H); 4.0 d.t (8H), 1.9 m (8H); 1.5–1.3 m (56–104H); 0.8 m (12H)

III-*n*: ^{1}H NMR spectrum (500 MHz; $CDCl_3$): 8.3 d.d (4H); 7.8 d (2H); 7.7 s (2H); 7.4 d.d (4H); 7.2 d (1H); 7.16 s (1H); 7.1 d (1H); 6.9 d (2H); 4.0 d.t (8H), 2.3 s (3H); 1.9 m (8H); 1.5–1.3 m (56–120H); 0.8 m (12H).

IV-*n*: ^{1}H NMR spectrum (400 MHz; $CDCl_3$): 8.3 m (4H); 7.8 d.d (2H); 7.7 d (2H); 7.3 m (4H); 7.1 s (2H); 6.9 d (2H); 4.0 d.t (8H), 2.2 s (6H); 1.9 m (8H); 1.5–1.3 m (56–88H); 0.9 m (12H).

V-12: No data were obtained as the compound was unstable in $CDCl_3$ and CD_2Cl_2.

VI-12: ^{1}H NMR spectrum (400 MHz; $CDCl_3$): 8.3 m (4H); 7.8 d.d (2H); 7.65 d (2H); 7.4 m (4H); 7.2–7.1 m (4H); 6.9 d (2H); 4.0 d.t (8H), 2.6 t (2H); 1.9 m (8H); 1.5–1.3 m (100H); 0.9 m (12H).

VII-*n*: ^{1}H NMR spectrum (270 MHz; $CDCl_3$): 8.3 m (4H); 7.8 d.d (2H); 7.6 d (2H); 7.4 m (4H); 7.1 s (2H); 6.9 d (2H); 4.0 d.t (8H), 1.9 m (8H); 1.5–1.2 m (56–88H); 0.9 m (12H)

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REFERENCES

1. Nguyen, H.-T., Destrade, C., and Malthête, J., *Adv. Mater*., 1997, vol. 9, no. 5, p. 375.
2. Nguyen, H.-T., Destrade, C., and Malthête, J., *Phasmids and Polycatenar Mesogens. Handbook of Liquid Crystals*, Demus, D., Goodby, J.W., Gray, G.W., Spiess, H.W., and Vill, V., Eds., Weinheim: Wiley-VHC, 1998, vol. 2B, ch. XII, p. 865.
3. Hoag, B.P. and Gin, D.L., *Adv. Mater*., 1998, vol. 10, p. 1546; Isoda, K., Yasuda, T., and Kato, T., *J. Mater. Chem*., 2008, vol. 18, p. 4522; Lincker, F., Bourgun, P., Masson, P., Didier, P., Gui-doni, L., Bigot, J.-Y., Nicoud, J.-F., Donnio, B., and Guillon, D., *Org. Lett*., 2005, vol. 7, p. 1505; Eichhorn, S.H., Paraskos, A.J., Kishikawa, K., and Swager, T.M., *J. Am. Chem. Soc*., 2002, vol. 124, p. 12742; Matraszek, J., Mieczkowski, J., Pociecha, D., Gorecka, E., Donnio, B., and Guillon, D., *Chem. Eur. J*., 2007, vol. 13, p. 3377; Rowe, K.E., and Bruce, D.W., *J. Mater. Chem*., 1998, vol. 8, p. 331; Cardinaels, T., Ramaekers, J., Nockemann, P., Driesen, K., Van Hecke, K., Van Meervelt, L., De Feyter, S., Wang, G., Fernandez Iglesias, E., Guillon, D., Donnio, B., Binnemans, K., and Bruce, D.W., *Soft Matter*., 2008, vol. 4, p. 2172.
4. Guillon, D., Heinrich, B., Ribeiro, A.C., Cruz, C., and Nguyen, H.T., *Mol. Cryst. Liq. Cryst*., 1998, vol. 317, p. 51.
5. Donnio, B., Heinrich, B., Allouchi, H., Kain, J., Diele, S., Guillon, D., and Bruce, D.W., *J. Am. Chem. Soc*., 2004, vol. 126, p. 15258.
6. Praefcke, K., Holbrey, J.D., and Usol'tseva, N., *Mol. Cryst. Liq. Cryst*., 1996, vol. 288, p. 189.
7. Smirnova, A.I. and Bruce, D.W., *Chem. Commun*., 2002, vol. 2, p. 176.
8. Smirnova, A.I. and Bruce, D.W., *J. Mater. Chem*., 2006, vol. 16, p. 4299.
9. Attwood, T.K., Lydon, J.E., Hall, C., and Tiddy, G.J.T., *Liq. Cryst*., 1990, vol. 7, p. 657.
10. Donnio, B. and Bruce, D.W., *J. Mater. Chem*., 1998, vol. 8, p. 1993.
11. Tuffin, R.P., Toyne, K.J., and Goodby, J.W., *J. Mater. Chem*., 1996, vol. 6. N 8, p. 1271.
12. (a) Nguyen, H.T., Destrade, C., and Malthête, J., *Liq. Cryst*., 1990, vol. 8, p. 797; (b) Malthête, J., Nguyen, H.T., and Destrade, C., *Liq. Cryst*., 1993, vol. 13. N 2, p. 171.
13. Fazio, D., Mongin, C., Donnio, B., Galerne, Y., Guillon, D., and Bruce, D.W., *J. Mater. Chem*., 2001, vol. 11, p. 2852.
14. Rourke, J.P., Fanizzi, F.P., Salt, N.J.S., Bruce, D.W., Dunmur, D.A., and Maitlis, P.M., *J. Chem. Soc., Chem. Commun*., 1990, p. 229.
15. Mongin, C., Donnio, B., and Bruce, D.W., *J. Am. Chem. Soc*., 2001, vol. 123, p. 8426.
16. Cardinaels, T., Ramaekers, J., Nockemann, P., Driesen, K., Van Hecke, K., Van Meervelt, L., De Feyter, S., Wang, G., Fernandez Iglesias, E., Guillon, D., Donnio, B.,

Binnemans, K., and Bruce, D.W., *Soft Matter*., 2008, vol. 4, p. 2172.

17. Usol'tseva, N., Praefcke, K., Smirnova, A., and Blunk, D., *Liq. Cryst*., 1999, vol. 26, p. 1723.
18. Weissflog, W., *Laterally Substituted and Swallow-Tailed Liquid Crystals. Handbook of Liquid Crystals,* Demus, D., Goodby, J.W., Gray, G.W., Spiess, H.W., and Vill, V., Eds., Weinheim: Wiley-VHC, 1998, vol. 2B, ch. XI, p. 835.
19. Hird, M., *Chem. Soc. Rev*., 2007, vol. 36, p. 2070.
20. Chan, W.-K., Chen, Y., Peng, Z., and Yu, L., *J. Am. Chem. Soc*., 1993, vol. 115, p. 11735.
21. Fujita, S. and Sano, K., *J. Org. Chem*., 1979, vol. 44, no. 15, p. 2647.