Invited Article

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Invited Article

Phasmids and polycatenar mesogens

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Several series of phasmids and biforked mesogens or more generally of polycatenar mesogens, i.e. rod-like core mesogens ending in six, five, four or three aliphatic chains (respectively hexa-, penta-, tetra- and tricatenars) are reviewed. According to the number and positions of the aliphatic chains, lamello-columnar, columnar, cubic, smectic and nematic phases appear.

1. Introduction

It is well-established that the symmetry of thermotropic mesophases is widely determined by the global shape of the mesogenic molecules [1]. For example rod-like molecules form lamellar mesophases [2] (except amphiphilic molecule such as neat soaps, which can also exhibit columnar mesomorphism [3]) while disc-like [4, 5] or cone-shaped [6] molecules form columnar mesophases. So, it was interesting to examine the mesomorphism of low molecular weight hybrid molecules with a rod-like rigid core ending in one or two half-disc-shaped moieties. The recent discovery of such mesogens, that is the phasmids [7] which fill the gap between rod-like and disc-like mesogenic compounds, allows us to enhance our knowledge of the relationships between molecular architecture and mesomorphic properties. Polymers containing such hybrid mesogenic units have also been investigated [37–39] but the present review only treats low molar mass liquid crystals.

Because of the large number of series which have been studied and the exceptional polymorphism encountered [7–23], it was a good opportunity to summarize every available data on this topic. In fact, this large number of homologous compounds allows easy comparisons between the molecule structure and mesomorphic properties. In particular we have explored the influence of the number and positions—*meta* and/or *para*—of the aliphatic chains on the terminal benzene rings.

2. Nomenclature

Originally, the term phasmids applied to rod-like mesogens ending in two trialkyloxyphenyl groups because of the similarity of their structure with a six-legged

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stick-like insect named phasma [7]. Taking into account the number of possible combinations, i.e. anchoring points of the aliphatic chains in *ortho*, *meta* and *para* positions, we first propose a nomenclature related to the number and positions of the aliphatic chains.

Six chain compounds are named hexacatenar mesogens or hexacatenars (from the Latin catena for chain). In the same way, the five, four and three chain compounds are labelled penta-, tetra- and tricatenar mesogens or penta-, tetra, and tricatenars, respectively. To avoid any confusion, it must be emphasized that the term catenar is reserved for mesogens with a clear rod-like core (i.e. an elongated polyaromatic part with rings connected in the *para* positions) and normal aliphatic chains only grafted on the two terminal benzene rings. Only the polycatenar mesogens thus defined are reviewed in this invited article. Consequently, our definition excludes disc-like mesogens, fused twins [24], bent elongated mesogens [25] and rod-like mesogenic compounds with a lateral chain on a non-terminal benzene ring [26, 27] or bearing a branched chain on a terminal benzene ring [28, 29]. Nevertheless, some disc-like mesogens with a two-fold symmetry such as rufigallol hexaalkanoates [30], tetra-alkanoates of ellagic acid [31] or cello-oligosaccharides derivatives [32] are at the boundary between disc-like and polycatenar mesogens.

2.1. *Hexacatenar mesogens*

Two different types of hexacatenar compounds are known: (i) three chains in the *meta*, *para* and *meta* positions at each end (in short 3(*mpm*) + 3(*mpm*)) and (ii) [33] three chains in the *ortho*, *meta* and *para* positions at each end (in short 3(*omp*) + 3(*omp*)).

$$R = n - C_n H_{2n+1} O-$$

3(mpm) + 3(mpm)

3(omp) + 3(omp)
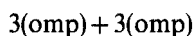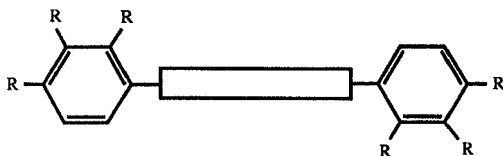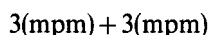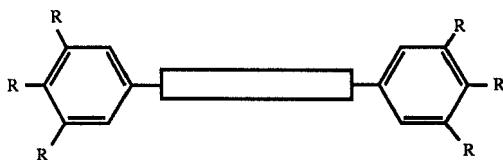
2.2. *Pentacatenar mesogens*

Two isomers of pentacatenar mesogens have been considered: three chains (*meta*, *para*, *meta*) at one end and two chains (*meta*, *para* or *meta*, *meta*) at the other end (in short: 3(*mpm*) + 2(*mp*) and 3(*mpm*) + 2(*mm*)).
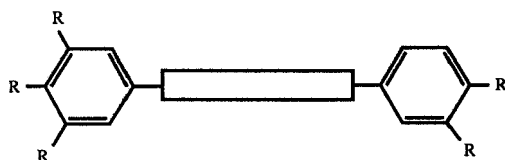
3(mpm) + 2(mp)
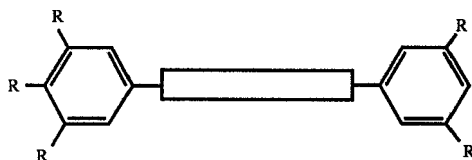
3(mpm) + 2(mm)

2.3. *Tetracatenar mesogens*

Four isomers have been studied (in short: 3(*mpm*) + 1(*p*), 2(*mp*) + 2(*mp*), 2(*mp*) + 2(*mm*) and 2(*mm*) + 2(*mm*)).

3(mpm) + 1(p)

2(mp) + 2(mp)

2(mp) + 2(mm)
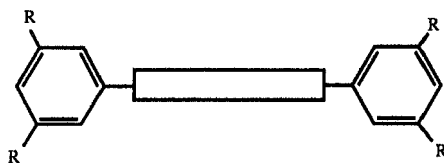
2(mm) + 2(mm)

2.4. *Tricatenars*

In this case three mesogenic isomers have been investigated: 2(*mp*) + 1(*p*), 2(*mm*) + 1(*p*) and 2(*op*) + 1(*p*).
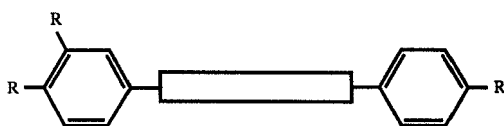
2(mp) + 1(p)
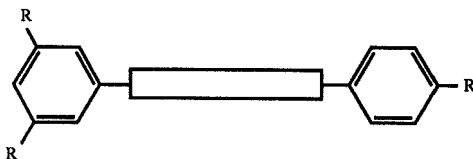
2(mm) + 1(p)
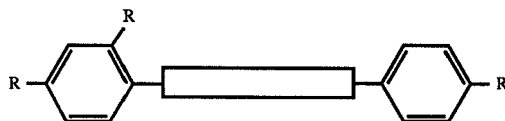
2(op) + 1(p)

The classical rod-like mesogens are clearly bicatenar compounds 1(*p*) + 1(*p*).
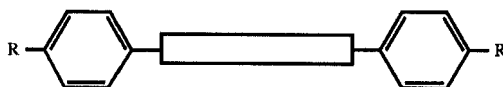
1(p) + 1(p)

3. Mesomorphic properties

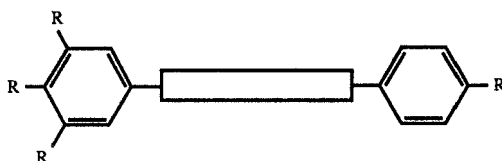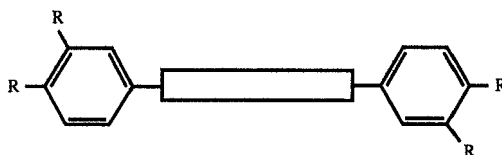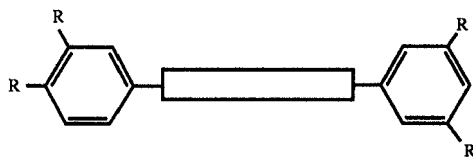Many polycatenar mesogens exhibit columnar mesophases which might be termed D phases like those of disc-like compounds [5]. However, considering first the geometrical anisotropy of polycatenars and then the structure of their columnar mesophases which do not consist of the common stacking of molecular discs, we have decided in favour of using another symbol to avoid any confusion. In so far as the first examples of such mesophases were observed in the so-called phasmids [7], we shall keep the chosen symbol Φ to label these columnar mesomorphic arrangements. In contrast, we use the traditional nomenclature for the lamellar (S) and nematic (N) mesophases.

3.1. *Hexacatenar mesogens or phasmids: 3(mpm) + 3(mpm)*

Beside some series of hexacatenar mesogens 3(*omp*) + 3(*omp*), in which biaxial nematic properties have been claimed [33], hexacatenar mesogens 3(*mpm*) + 3(*mpm*) have been especially studied. In most cases the molecule **1** is symmetric, consequently the linkages *Y* and *Z* correspond to inverted *X* and *W* respectively on the right hand side of the ring A. The first studies were performed on phasmids **2** with two different chain

1

$R = n\text{-}C_nH_{2n+1}O$

$W = -COO-$

$X = -N=CH-,\ -OCO-,\ -OCH_2-$

$Y = -CH=N-,\ -COO-,\ -CH_2O-$

$Z = -OCO-$
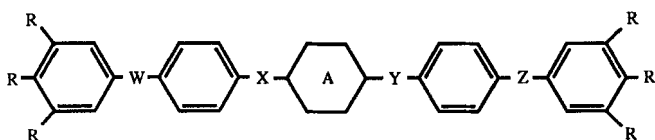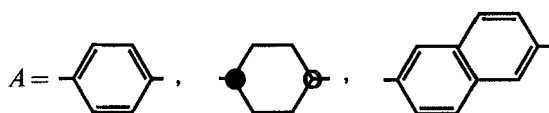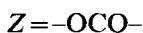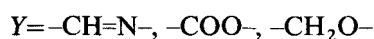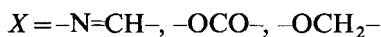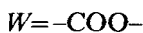
Table 1†.   Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of phasmids **2** [7, 11].

$R = n\text{-}C_nH_{2n+1}O-$

2

n	C		Φ_{ob}		Φ_h		I
7	●	80	—		●	82	●
12	●	70	●	81·5	●	92	●
		65·2		0·25		5·85	
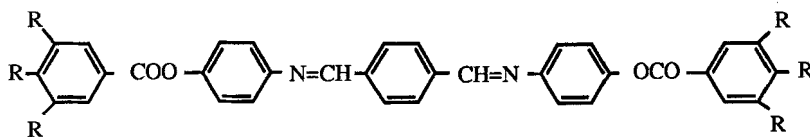
† C = crystal; Φ_{ob} = phasmidic phase with an oblique two dimensional lattice; Φ_h = phasmidic phase with a hexagonal two dimensional lattice; ●: the phase exists; —: the phase does not exist. Lattice constants ($n = 12$): Φ_{ob}, $a = 39\cdot2$ Å, $b = 23$ Å; Φ_h, $a = 45$ Å.

lengths (see table 1): the short chain derivative only exhibits a hexagonal columnar phase while the longer gives the first evidence of a transition between an oblique and a hexagonal mesophase.

The homologous series **3** and **4** have been synthesized so as to study the influence of the chain length and rigidity of the central part on the mesomorphic properties (see tables 2 and 3). Compounds **3** present the same mesomorphism as compounds **2** but in this case the oblique mesophase is observed with short chains. Moreover the polymorphism is less rich than the first: we have only one mesophase for each compound. This behaviour can be correlated with the rigidity of the central part; as a matter of fact compounds **4** having a cyclohexane instead of a benzene ring show only one monotropic mesophase.

Table 2.   Transition temperatures (°C) of phasmids **3**.

$$R = n\text{-}C_nH_{2n+1}O-$$

3
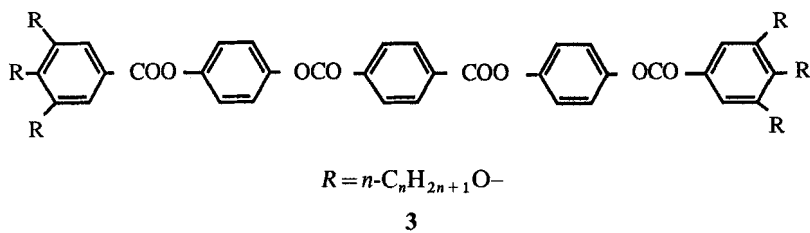
n	C		Φ_{ob}		Φ_h		I
7	●	82	●	87	—		●
8	●	69	●	87	—		●
9	●	73	●	87	—		●
10	●	60	●	90	—		●
11	●	83	—		●	92·5	●
12	●	88	—		●	94	●
13	●	90	—		●	94	●
14	●	85	—		●	94	●

Table 3.   Transition temperatures (°C) of phasmids **4**.

$$R = n\text{-}C_nH_{2n+1}O-$$

4
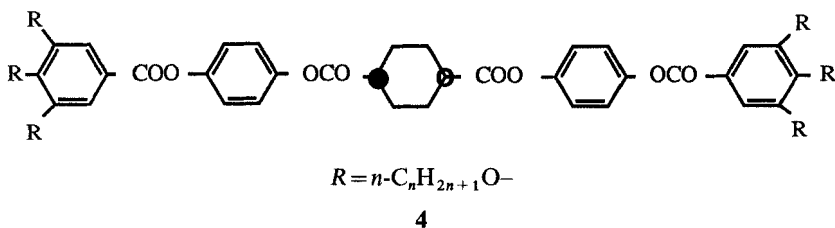
n	C		Φ_h†		I
7	●	86	(●	60)	●
8	●	71	(●	66)	●
9	●	76	(●	67·5)	●
10	●	79	(●	77)	●
11 [12]	●	85	(●	80)	●
12 [12]	●	88	(●	82)	●
13 [12]	●	92	(●	82)	●
14	●	88	(●	75·5)	●

† Only identified from optical textures.

When we replace the central ester linkages by the more flexible $-CH_2O-$ groups, a fugitive metastable Φ_h phase is obtained. For example, with compound **5** a Φ_h phase is observed with rapid cooling. On the other hand, compound **6** displays a stable Φ_h phase over a larger temperature range than the series **2** and **3**.

$$R=n\text{-}C_{10}H_{21}O-$$

5

C 84°C I

$$R=n\text{-}C_{10}H_{21}O-$$

6
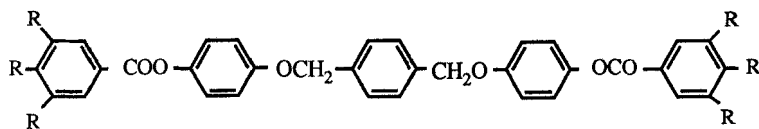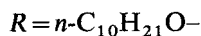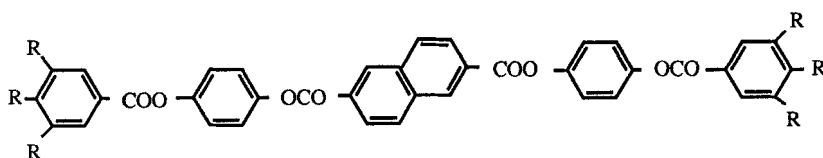
C 75°C Φ_h 110°C I

It seems that the number of aromatic or alicyclic rings cannot be lower than five to obtain mesomorphic properties, but beside some unsuccessful attempts with four or less rings, a peculiar case is worth reporting: the compound **7** [9, 14] displays a columnar phase with a four benzene ring core ending in six aliphatic chains grafted by means of benzyloxy groups, i.e. in two large triangular parts, nearly half-super-discs, namely 3,4,5-tris(4-*n*-dodecyloxybenzyloxy)benzoyloxy groups (DOBOB in short).

$$R = n\text{-}C_{12}H_{25}O \quad CH_2O-$$
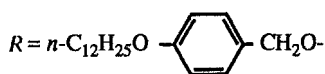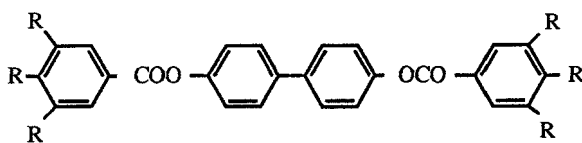
7

Some features are to be emphasized:

In spite of the core length, the clearing points are surprisingly low (about 80–90°C). We can attribute this weak stability of the phases to the large number (six) of the aliphatic chains and the lateral (*meta*) positions for four of them.

The only mesomorphic phases observed within the hexacatenar series are columnar or ribbon mesophases (see tables 1 to 3). We note that in this case we have four chains in *meta* positions and only two in *para*.

According to some dilatometric and X-ray diffraction measurements [11], it has been assumed that in the hexagonal columnar phase Φ_h the hexacatenar molecules may be associated into clusters; the column section being formed by three molecules on an average.

With other derivatives a lamello-columnar (or ribbon) phase is observed, alone (see table 2, $7 \leqslant n \leqslant 10$) or below a Φ_h phase (see tables 1 and 2). This mesophase has a lamellar structure with a equal to the thickness of the lamella, and b equal to the distance between two columns, the axes of which are parallel to the lamella. The columns are arranged according to an oblique (Φ_{ob}) two dimensional lattice [7].

3.2. *Pentacatenar mesogens*

A few pentacatenar mesogens have been reported. For example, in compounds **8** [3(*mpm*) + 2(*mp*)] and **9** [3(*mpm*) + 2(*mm*)] only a hexagonal columnar phase is observed.

$$R = n\text{-}C_{12}H_{25}O\text{--}, \ R' = n\text{-}C_{10}H_{21}O\text{--}; \ C \ 75°C \ \Phi_h \ 132°C \ I \ [12]$$

8

$$R = n\text{-}C_{12}H_{25}O\text{--}; \ C \ 25°C \ \Phi_h \ 86°C \ I$$
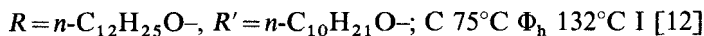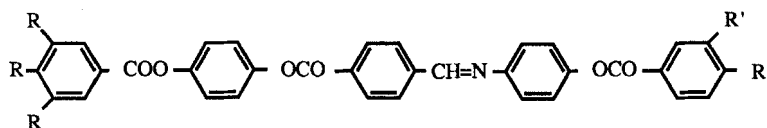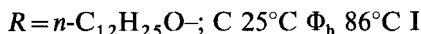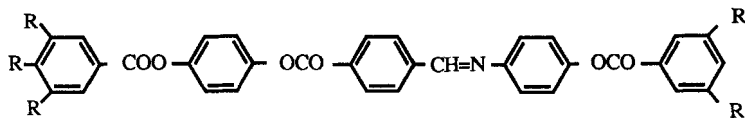
9

3.3. *Tetracatenar mesogens*

As previously described tetracatenar mesogens correspond to four combinations.

3.3.1. *3(mpm) + 1(p)*

Tetracatenar **10** only displays a cubic phase: C 79°C Cub 146°C I, while compounds such as **11**, with one DOBOB group, exhibit a hexagonal (**11a, b**) [9, 14] or a nematic phase (**11c, d**) with apparent biaxial properties [9, 10].

$$R = n\text{-}C_{12}H_{25}O\text{--}, \ R' = n\text{-}C_{10}H_{21}O\text{--}$$

10

11a

$R = n\text{-}C_{12}H_{25}O$ —〈 〉— CH_2O-

$R' =$ —〈 〉— $OC_{12}H_{25}$

b =

c = —〈 〉—〈 〉— OCO —〈 〉— OC_8H_{17}

d = —〈 〉—〈 〉— OCO —〈 〉— $OC_{12}H_{25}$
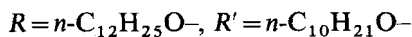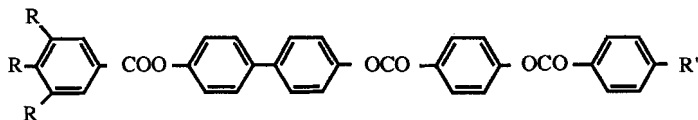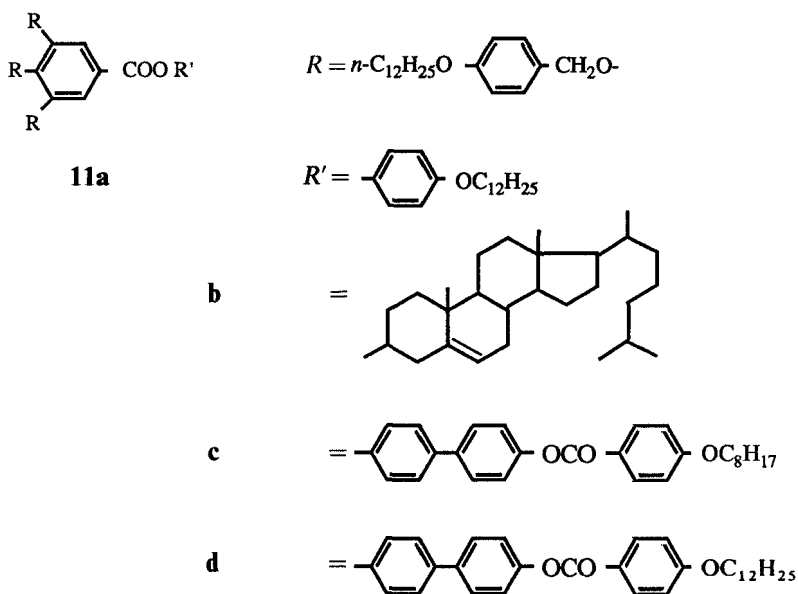
3.3.2. $2(mp) + 2(mp)$

Several series of such biforked mesogens have been reported [8, 13, 16, 17, 20]. They correspond to the general formula **12**. The striking feature of these compounds is the presence of both lamellar and columnar phases, as well as nematic and cubic phases. Several examples corresponding to different values of W, X, Y, Z and A, as well as various chain lengths are given in tables 4 to 7.

$$R = n\text{-}C_n H_{2n+1} O-$$

12
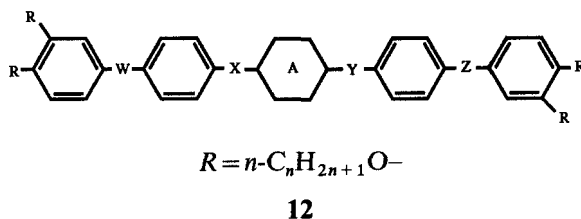
The polymorphism within the series **13** (see table 4) is strongly dependent on the alkyl chain length. Short chain derivatives ($n = 6$ to $n = 8$) exhibit two mesophases unambiguously identified by their optical textures as a lamellar phase of smectic C type and a nematic phase. The X-ray patterns indicate that the tilt angle reaches $50°$ in the S_C phase. Derivatives with $n = 9$ and 10 show only a S_C phase over a large temperature range. In contrast, derivatives with $n = 11$ and 12 exhibit an interesting polymorphism with a lamellar phase (S_C) at a lower temperature and a columnar phase (Φ_h) at a higher temperature is realized in both cases via a lamello-columnar mesophase (Φ_{ob}) with the lattice constants $a = 33 \cdot 1$ Å, $c = 59 \cdot 5$ Å and $\beta = 145°$ (derivative with $n = 11$). The thickness of a ribbon ($c \sin \beta$) is equal to the layer thickness of the S_C phase at a lower temperature (nearly $34 \cdot 1$ Å), while the lattice constant of the hexagonal columnar phase is $46 \cdot 9$ Å [13], a value very similar to that obtained with the corresponding phasmid $3(mpm) + 3(mpm)$, for which $a = 45$ Å for the derivative with $n = 12$ [7]. Finally, the longest chain homologues $n = 14$, exhibit only one mesomorphic phase (Φ_h).

For the compounds of table 5, a similar behaviour is observed for short chains: S_C and N mesophases while for long chains a two dimensional rectangular mesophase

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Table 4. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of tetracatenars **13** [13].

$$R = n\text{-}C_nH_{2n+1}O-$$

13
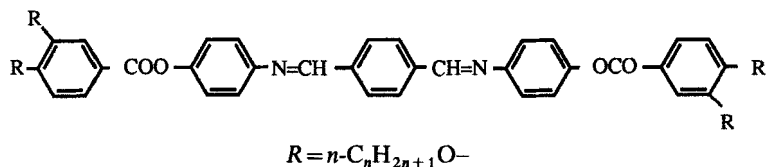
n	C		S$_C$		Φ$_{ob}$		Φ$_h$		N		I
6	•	160 *28·0*	•	200 *6·18*	—		—		•	240 *1·04*	•
7	•	138	•	199·5	—		—		•	223·5	•
8	•	137 *64·8*	•	198·5 *6·48*	—		—		•	206·5 *0·67*	•
9	•	130	•–	191	—		—		—		•
10	•	125 *58·1*	•	185 *5·73*	—		—		—		•
11	•	129 *64·4*	•	154 *0·42*	•	170 *1·71*	•	187 *5·14*	—		•
12	•	127·5 *71·9*	•	128·5 *0·83*	•	161 *1·25*	•	186 *5·52*	—		•
14	•	123 *88·6*	—		—		•	176 *5·94*	—		•

Table 5. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of tetracatenar **14** [20].

$$R = n\text{-}C_nH_{2n+1}O-$$

14
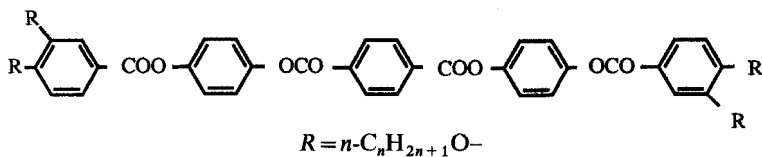
n	C		S$_C$		Φ$_r$		N		I
6	•	195 *52·2*	—		—		•	217 *1·07*	•
7	•	191·5 *51·7*	(•	179·5) *7·10*	—		•	205·5 *0·95*	•
8	•	175 *39·9*	•	182 *7·07*	—		•	196·5 *0·89*	•
9	•	162 *33·1*	•	179·5 *6·55*	—		•	183·5 *0·84*	•
10	•	156 *60·6*	•	176 *7·68*	—		—		•
11	•	151 *53·4*	•	170·5 *6·44*	—		—		•
12	•	148 *65·9*	•	167 *6·28*	—		—		•
13	•	145·5 *67·1*	—		•	163 *6·89*	—		•
14	•	142·5 *75·4*	—		•	162 *6·71*	—		•

occurs instead of a hexagonal one. A similar mesomorphism has been reported by Diele *et al.* [34] in series **15**.

$$n\text{-}C_6H_{13} \leqslant R \leqslant n\text{-}C_{16}H_{33}$$
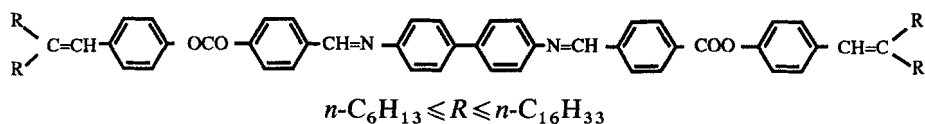
15

Although these compounds are not strictly speaking polycatenar mesogens, the analogy with our so-called tetracatenar derivatives is obvious.

Table 6 gives an example of a series in which a cubic mesophase has been demonstrated. Other examples will be found in [8, 16]. Let us emphasize that a hexagonal mesophase with a large lattice constant corresponding to twice the molecular length has been observed on cooling from the isotropic phase before the appearance of the cubic phase.

Table 6. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of tetracatenars **16** [20].
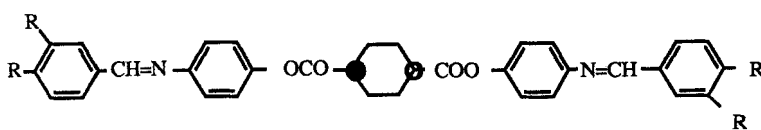
$$R = n\text{-}C_nH_{2n+1}O\text{--}$$

16

n	C		S_C		Cub		Φ_h		I
7	●	152	●	183	—		—	—	●
8	●	148	●	176	—		—		●
		81·9		*5·73*					
9	●	146·5	●	168·5	—		—		●
		81·2		*5·49*					
10†	●	144	●	156	●	165	—		●
		93·5		*2·30*		*3·00*			
11‡	●	144	●	146	●	163	—		●
		102·8		*2·42*		*3·02*			
12§	●	142	—		●	162	—		●
		106·7				*3·04*			
13	●	141	—		—		●	163	●
		94·1						*3·83*	
14	●	140	—		—		●	163	●
		127·7						*4·27*	

† On cooling: I 157°C S$_C$ 138°C C; ‡ on cooling: I 158°C Φ_h 147°C Cub 140°C S$_C$ 135°C C; § on cooling: I 160°C Φ_h 138°C C (the hexagonal columnar phase has a large lattice constant).

Table 7†.   Transition temperatures (°C) and enthalpies (kJ mol^{-1}) of tetracatenars **17** [16].

$$R = n\text{-}C_nH_{2n+1}O-$$

17
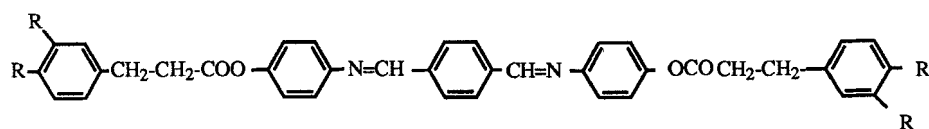
n	C		Φ_{rh1}		Φ_{rh2}		Φ_{hex}		Φ_{ob}		Φ_h		I
9	•	109 51·8	•	126	•	152	—		•	155 5·84	—			•
10	•	110 57·1	—		—		•	150	—		•	155 6·99	•
11	•	111 44·0	—		—		—		—		•	156 5·74	•
12	•	111 67·2	—		—		—		—		•	155·5 8·39	•
13	•	112 69·6	—		—		—		—		•	155·5 8·89	•
14	•	111·5	—		—						•	154	•

† Φ_{rh1} and Φ_{rh2}: rhombohedral mesophases; Φ_{hex}: hexagonal three dimensional mesophase.

3.3.3. 2(mp) + 2(mm)

Only one example (**18**) of this type of tetracatenar has been studied: C 78°C Φ_h 99°C I. On the other hand, no mesomorphic properties were observed with a –N=CH– instead of –CH=N– linkage (m.p. 124°C).
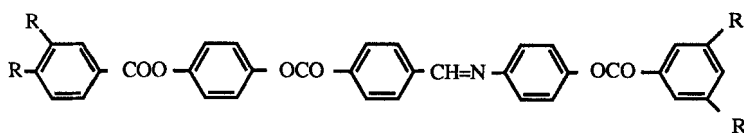
$$R = n\text{-}C_{12}H_{25}O-$$

18

3.3.4. 2(mm) + 2(mm)

A homologous series with a six benzene ring core **19** has been studied (see table 8) [13]. Within the series, only one type of mesophase has been detected by optical observations. The textures are fan shaped, with developable domains in every way similar to those of the Φ_h phase of tetracatenars 2(mp) + 2(mp). Despite the unusual length of the central rigid part, the transition temperatures are surprisingly low, a fact evidently connected with the *meta* position of all the alkoxy chains. Indeed, the homologous five benzene ring derivatives are isotropic at room temperature and somewhat difficult to isolate.

Table 8. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) or tetracatenars **19**.

$$R = n\text{-}C_nH_{2n+1}O-$$

19
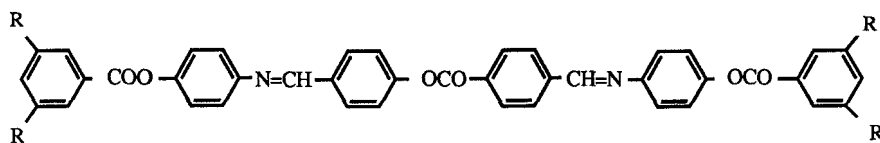
| n	C		Φ_h		I
7	●	110	(●	104)	●
8	●	96	●	112	●
10	●	76	●	110	●
11	●	68	●	116	●
		36·6		*2·72*	

3.4. *Tricatenar mesogens*

Several other mesogens of this type have been synthesized. They have a three benzene ring core and display the classical mesomorphic properties of rod-like mesogens. For instance compounds **20** and **21a–c** are smectogenic C and nematogenic, while when the chain is moved from the *meta* to the *ortho* position, the compound only becomes nematogenic.
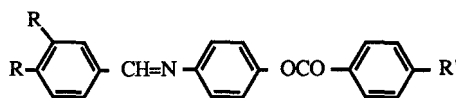
$$R = n\text{-}C_9H_{19}O-, \quad R' = n\text{-}C_7H_{15}O-; \quad C\,106°C\,(N\,104°C)\,I$$

20
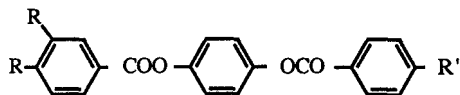
$$R' = n\text{-}C_9H_{19}-$$

21a $R = n\text{-}C_4H_9O-$ C 92°C N 93°C I

b $R = n\text{-}C_8H_{17}O-$ C 90°C (S$_C$ 82°C N 88°C) I

c $R = n\text{-}C_{12}H_{25}O-$ C 88°C (S$_C$ 82·5°C N 86°C) I [35]

Another interesting example is the five benzene ring tricatenar 2(*mm*) + 1(*p*) **22**, which exhibits a cubic phase over a large temperature range from 83 up to 172°C [18].
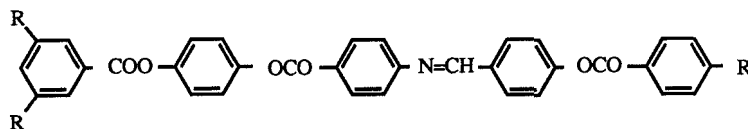
$$R = n\text{-}C_{12}H_{25}O-$$

22

4. Discussion

Taking into account this large number of results, we are now able to identify some general molecular features which determine the nature of the mesomorphism. The mesomorphic polymorphism is, by evidence, connected to the number of rings (core length) and also to the number, position and length of the aliphatic chains.

4.1. *Core length*

To obtain mesomorphic properties we need at least three benzene rings in our studies, and only in the case of dissymmetric molecules such as tricatenar mesogens [2(*mp*)+1(*p*) and 2(*op*)+1(*p*)] which exhibit smectic and nematic properties, like classical elongated molecules. It is clear that an increase of the number of chains directly grafted on to the core needs a parallel increase of core length to keep the mesomorphic properties. For example, with four chains, a minimum of a four ring core is necessary to obtain mesomorphic properties. With five and six chains, at least five rings are convenient for the mesomorphism. For instance, with three or four rings, only nematics or smectics are obtained, while with five and six rings, lamellar and/or columnar phases are obtained.

Now, if we focus our attention on the mesophase nature, it is clear that both core length and chains influence the existence of lamellar and columnar phases.

4.2. *Number and positions of chains*

We restrict this discussion to the five and six benzene ring compounds which exhibit the richest polymorphism. A few examples of *ortho* substitution, only leading to nematic properties, have been reported [33, 36]. This behaviour, doubtless associated with a core separation induced by the presence of a lateral chain, will not be detailed here.

Table 9 shows that when $Nm > Np$, columnar phases are obtained, when $Nm < Np$, lamellar phases are obtained, and when $Nm = Np$, a competition occurs between lamellar and columnar mesomorphism. In this situation, the chain length is crucial.

In conclusion we can point out some outstanding features. The molecular structure of polycatenars holds an intermediate position between the mesogenic discs and mesogenic rods, and the observed polymesomorphism is very similar to that of

Table 9. Comparison of the number and positions of aliphatic chains on mesomorphic properties.

	Number of chains in *meta* position (Nm)	*para* position (Np)	Lamellar phase	Cubic	Columnar phase
Hexacatenar	4	2	—	—	+
Pentacatenar	4	1	—	—	+
	3	2	—	—	+
Tetracatenar	4	0	—	—	+
	3	1	—	+	+
	2	2	+	+	+
Tricatenar	2	1	—	+	—
	1	2	+	—	—

lyotropic systems [40]. For example, in a homologous series two dimensional oblique or rectangular columnar phases or three dimensional cubic phases are inserted between lamellar and hexagonal columnar phases; in this case, the main area per aliphatic chain increases with temperature and chain length, corresponding to an increase of the curvature between the aromatic and the aliphatic moieties. For this reason the hexagonal columnar mesophase is always the high temperature one and is obtained directly from the isotropic liquid, and correlatively with two dense aliphatic ends (hexacatenars or phasmids and pentacatenars) a columnar phase occurs, when smectic and nematic phases appear by decreasing the number of aliphatic chains. The long chain tetracatenars $2(mp) + 2(mp)$ still exhibit a hexagonal columnar mesomorphism owing to their strong curvature in the core–chain interface. On decreasing the chain length, a smectic C phase appears to the detriment of the hexagonal phase: the passage between columnar and lamellar phases is realized via a lamello-columnar phase and/or a cubic phase. With short chain tetracatenars, i.e. with a weak curvature, as with a lower number of chains, classical mesomorphism occurs namely, smectic C and nematic phases. In any event the smectic C phase is the only observed lamellar mesophase in this kind of compound. Nevertheless, if the aliphatic chains are replaced by more polar chains (for example $-(CH_2)_nCN$) we can obtain a S_A phase. This last phase could be observed with penta- or even hexacatenar mesogens.

In all of the series reviewed the textures of columnar mesophases observed under the polarizing microscope are generally fan shaped (see [7] and [8]) and the birefringence decreases strongly from a smectic C to a columnar mesophase [12].

Concerning the disputed structural models of phasmidic columnar mesophases, we can emphasize the presence of more than one molecule in a slice of the column (two or
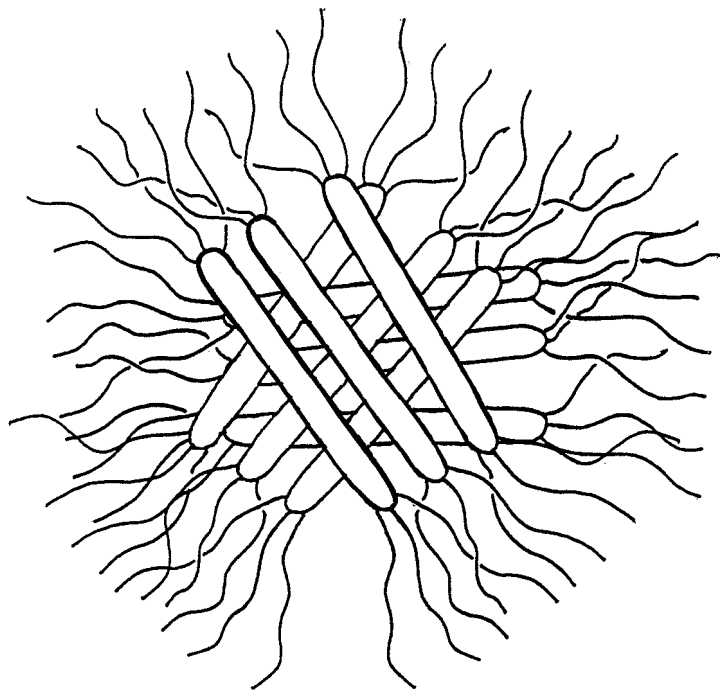
Schematic representation of a slice of a column in a columnar mesophase of phasmids.

three molecules for a six chain phasmid) [7, 11, 12, 14]. On the other hand, X-ray measurements on the crystalline phase of a biforked mesogen $17(n=12)$, which exhibits a hexagonal phase, shows a layered structure similar to that of a smectic C phase (molecular tilt angle of 60°) [21]. In addition, due to the bulky aliphatic chains, the interactions between cores are very weak perpendicular to the xz plane, i.e. along the future column axis parallel to the crystalline layers. So we can assume that above 112°C the aliphatic volume is large enough to allow the cores to twist slightly around the direction of weak coupling and realize an aliphatic crown which leads to columns (see the figure). Actually with respect to the weak transitional enthalpies between S_C–Φ_{ob}–Φ_h in various series (about 0·4–1·7 kJ mol^{-1}), it is difficult to believe that drastic structural changes occur between the different mesophases because of the permanence of an angle near to 60° in the various mesophases and in the crystalline state [21].

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