New biforked mesogen series

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New biforked mesogen series†

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Four new series of biforked mesogens derived from 3,4-dialkoxybenzoic acids or 3,4-dialkoxybenzaldehydes have been prepared and studied. These derivatives exhibit an interesting polymorphism in which both columnar and lamellar mesophases exist in the same series and in some cases in the same compound. The short chain derivatives exhibit a nematic and/or a smectic C phase but those with long chains display the hexagonal, rectangular or oblique columnar phases. In some of them, a centred cubic phase is found.

1. Introduction

Since the discovery of phasmids [1] and especially biforked mesogens [2] (the molecular structure of which is intermediate between classical rod-like and disc-like liquid crystals), the search for such new types of materials has accelerated together with structural studies on their columnar and lamellar mesophases [3–5]. If in the phasmids [1, 6] (or hexacatenar mesogens) we have only obtained a columnar phase, the biforked mesogens display nematic, lamellar, columnar, lamello-columnar and cubic phases in the same series. For this reason, our interest is now focused on this new kind of material and we report here four homologous series of biforked mesogens with the general formula:
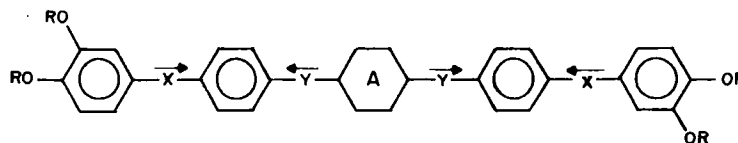
where $R = n\text{-}C_nH_{2n+1}(n = 6 \rightarrow 14)$

$\vec{X} = -COO-$ (I), $-CH = N-$ (II),

$\overleftarrow{X} = -OOC-$ (I), $-N = CH-$ (II),

$\vec{Y} = -OOC-;$ $\overleftarrow{Y} = -COO-$
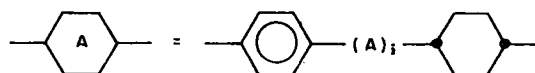
† Presented at the Eleventh International Liquid Crystal Conference, Berkeley, California, U.S.A., 30 June to 4 July 1986.

2. Synthesis

The two series I and II were prepared following the schemes 1 and 2:

IA,B
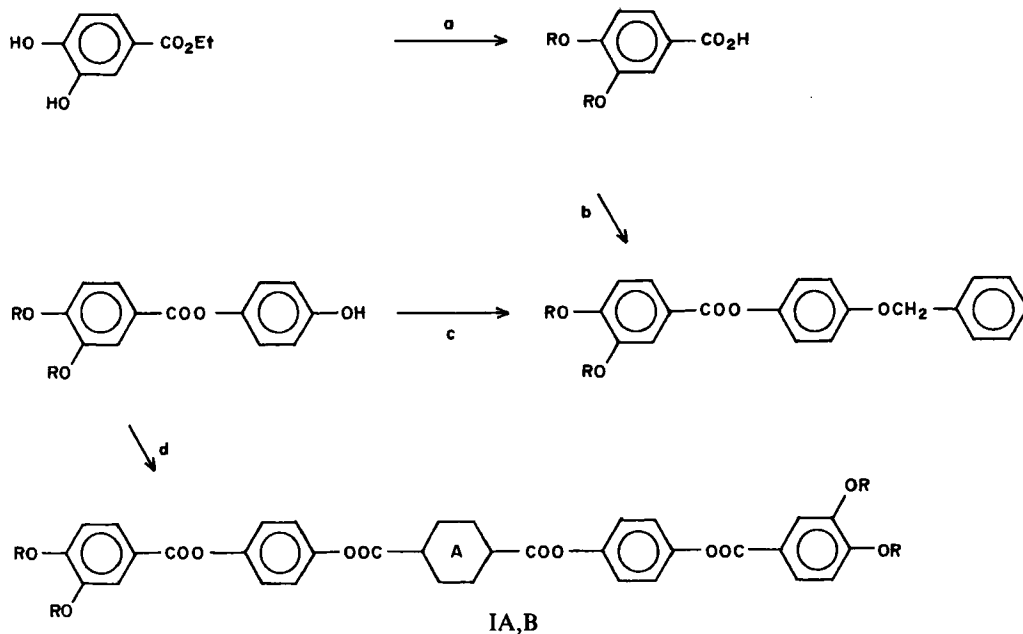
a, KOH, EtOH, RBr, HCl; *b* = SOCl₂, φCH₂OφOH pyridine; *c*, H₂, Pd/c, HOAc, RT; *d*,

HOOC—⟨A⟩—COOH, DCC, DMAP, CH₂Cl₂.

Scheme 1.

IIA,B

a, RBr, K₂CO₃, DMF; *b*, *p*-aminophenol, EtOH reflux; *c*, HOO—⟨A⟩—COOH, DCC,

DMAP, CH₂Cl₂

Scheme 2.

Figure 1.   A plot of the transition temperatures against n, the number of carbon atoms in the alkoxy chain of IA.

3.   Results and discussion
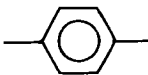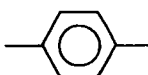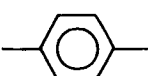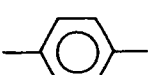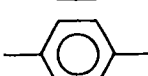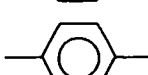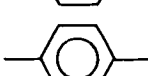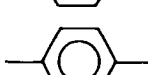
All of the compounds prepared are mesogenic. Their phase transitions were studied by both polarizing microscopy (equipped with a Mettler FP 5) and different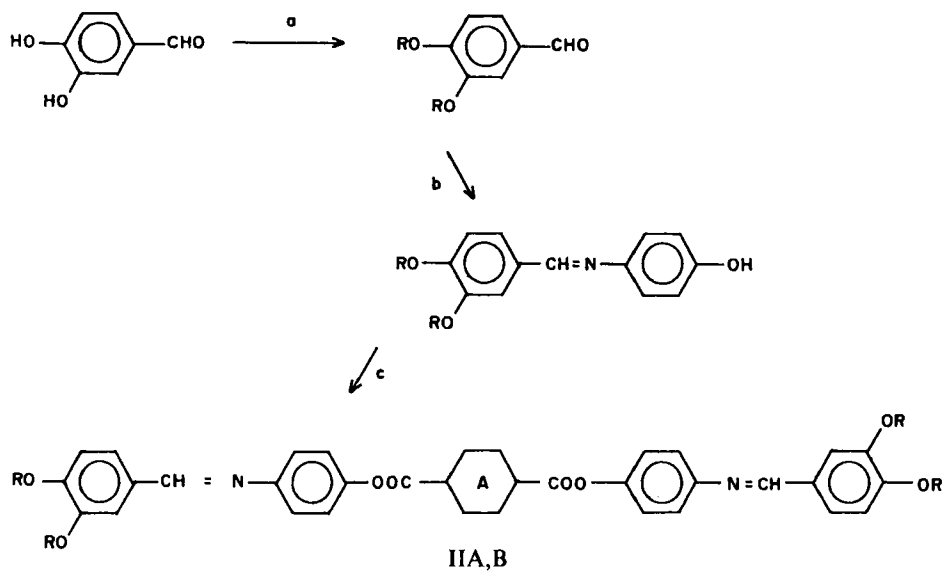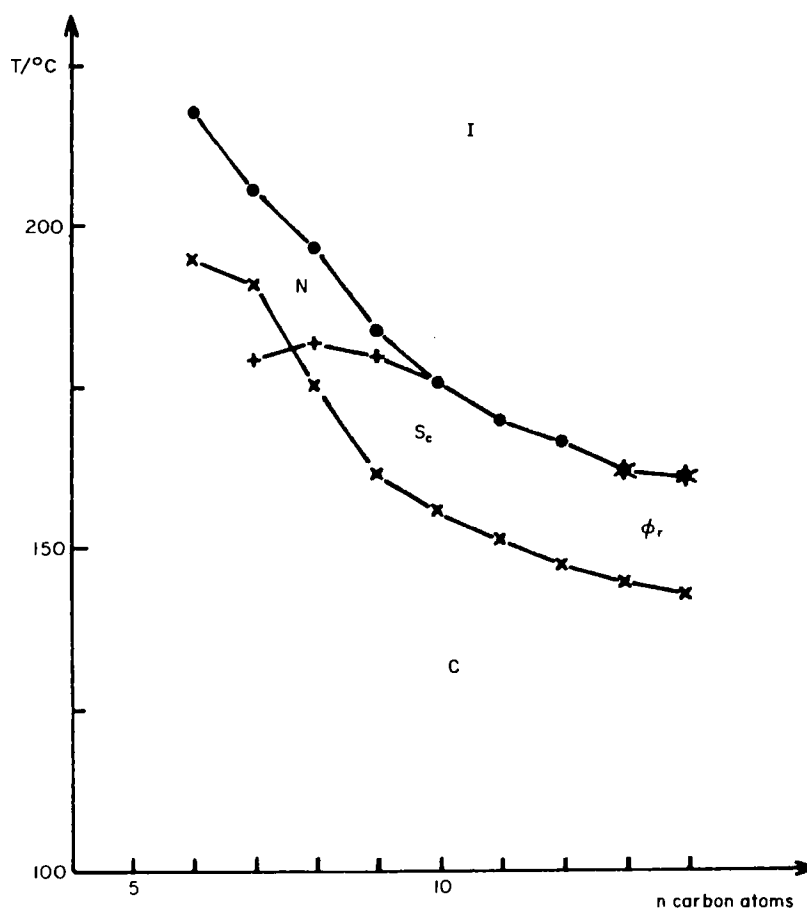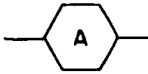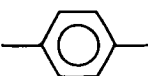ial scanning calorimetry (Perkin Elmer DSC 7). The transition temperatures and types of mesophases are given in tables 1 to 4.

3.1.   *Microscopic studies*
Series IA (*see figure 1 and table 1*)

The first compound of this series ($n = 6$) exhibits only a nematic phase with characteristic marbled or schlieren textures (see figure 2 (*a*)). In addition to this nematic phase, a smectic C phase is observed with broken fan shaped or schlieren textures in the three next compounds (see figure 2 (*b*)) ($n = 7-9$). From $n = 10$ the nematic phase disappears and we only observed the lamellar phase (S_C) in three compounds ($n = 10-12$). When the paraffinic chains are long enough to fill the space around the rigid part of the molecules the compounds display columnar phases. In this series, the columnar phase is the first centred rectangular columnar phase (ϕ_r) [15] observed in polycatenar mesogens. Its texture is similar to that of a hexagonal column phase but it is biaxial (see figure 2 (*c*)).

Table 1. The transition temperatures (°C) and enthalpies (kJ mol^{-1}) of compounds IA.

	n	C		S_C		ϕ_r		N		I
	6	•	195 52·22	–		–		•	217 1·07	•
	7	•	191·4 51·71	•	(179·5) 7·10	–		•	205·5 0·95	•
	8	•	175 39·91	•	182·2 7·07	–		•	196·7 0·89	•
	9	•	161·8 33·10	•	179·6 6·55	—		•	183·4 0·84	•
	10	•	155·8 60·65	•	176·2 7·68	—		—		•
	11	•	150·8 58·43	•	170·3 6·44	—		—		•
	12	•	148 65·86	•	167 6·28	—		—		•
	13	•	145·4 67·10	—		•	163 6·89	—		•
	14	•	142·6 75·36	—		•	162 6·71	—		•

Series IB (see figure 3 and table 2)

With a more flexible central ring (cyclohexyl) the compounds of series IB display the smectic C phase in all derivatives ($n = 6 \to 14$). In addition to this S_C phase, a nematic phase is observed in the two shortest paraffinic chain derivatives ($n = 6, 7$). On the other hand with long chains ($n = 12 \to 14$), the compounds exhibit S_C and hexagonal columnar phases (ϕ_h). The lattice spacing (a) of this hexagonal phase is 40·7 Å (for $n = 13$) and 50·3 Å (for $n = 14$). This uniaxial mesophase has wide developable domains (see figure 4).

Series IIA (see figure 5 and table 3)

Within the series IIA and IIB the X carboxylate group (-COO-) has been replaced by a more rigid -CH=N- linkage. All derivatives of the series IIA ($n = 7 \to 14$) do not form the nematic phase. In contrast the S_C phase is observed in three compounds ($n = 7-9$). The layer thickness of the S_C phase is 31·6 Å (for $n = 7$) while the

Figure 2. Optical textures: (a) 190° C nematic phase, (b) 180° C smectic C phase of IA ($n = 8$) (c) 160°C rectangular columnar phase of IA ($n = 14$).
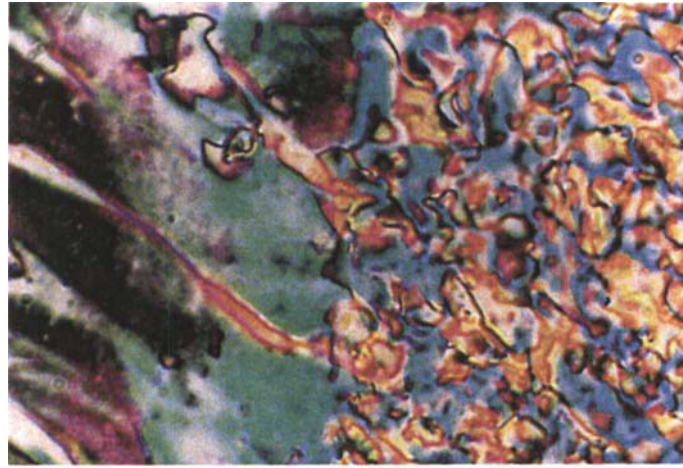
(a)
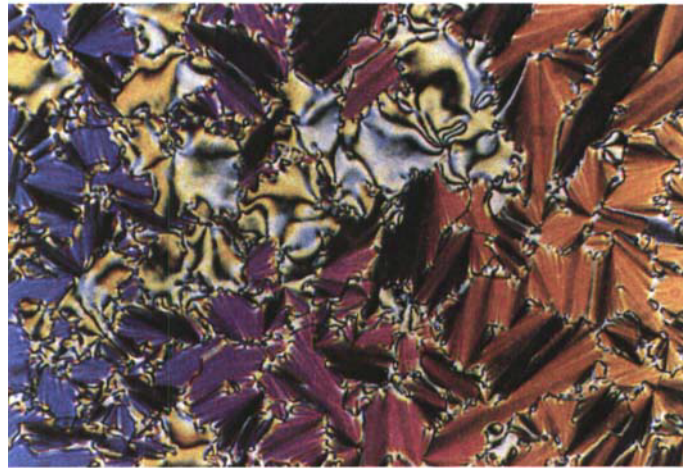
(b)

(c)
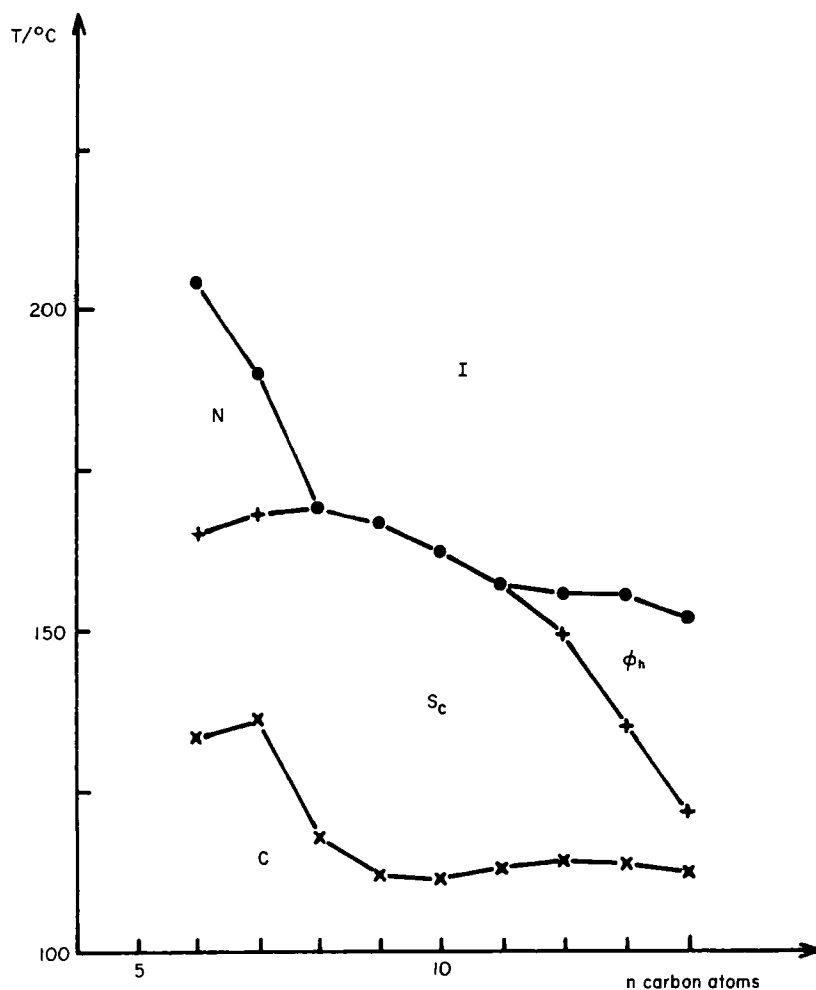
Figure 3. A plot of the transition temperatures against n, the number of carbon atoms in the alkoxy chain of IB.

molecular length is 55 Å, this phase with a strongly birefringent schlieren texture has a very high tilt angle of 50–60°. This tilt angle is higher than that of classical rod-like liquid crystals which exhibit the same sequence C S_C N I (40–50°) and even higher than that with the sequence C S_C S_A N I (10–30°). From $n = 10$ the hexagonal columnar phase appears, at first with an unknown phase like ($n = 10, 11$) and finally alone ($n = 12 \rightarrow 14$). The $\phi_?$ phase is more complexes than ϕ_{ob} [15]; it has striated and large fan-shaped textures (see figure 6). The normal hexagonal columnar phase has a lattice parameter varying from 45·9 Å (for $n = 10$) to 50·3 Å (for $n = 14$). We can compare this to the lattice constant of the hexagonal ϕ_h phase of phasmids [6, 14]:

$n = 11$, $a = 43·75$ Å,
$n = 12$, $a = 43·90$ Å,
$n = 13$, $a = 45·90$ Å
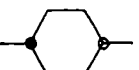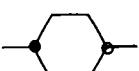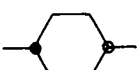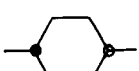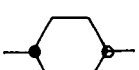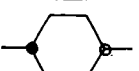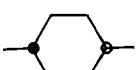
Table 2. The transition temperatures (°C) and enthalpies (kJ mol^{-1}) of compounds IB.

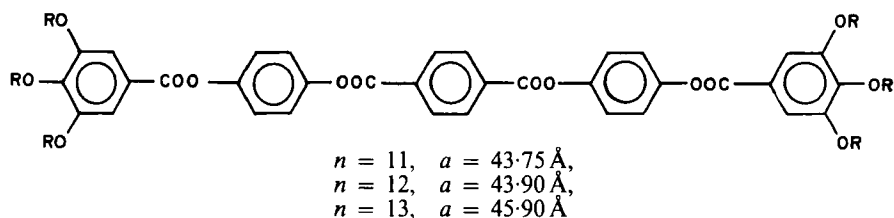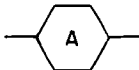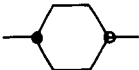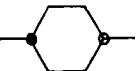| A	n	C	S_C	ϕ_r	N	I
	6	● 134 / 42·22	● 165 / 6·46	—	● 203·4 / 0·88	●
	7	● 136 / 52·33	● 168 / 6·73	—	● 190 / 1·02	●
	8	● 118 / 55·52	● 169 / 6·78	—	—	●
	9	● 111·6 / 41·88	● 167 / 7·92	—	—	●
	10	● 111 / 46·21	● 163 / 7·48	—	—	●
	11	● 113·3 / 50·88	● 157·4 / 6·34	—	—	●
	12	● 113 / 57·33	● 149 / 2·34	● 155·6 / 3·95	— ●	
	13	● 114 / 55·19	● 134·5 / 2·58	● 155·7 / 4·34	—	●
	14	● 122·6 / 60·01	● 121·7 / 2·82	● 152 / 4·24	—	●

The distance between two columns does not depend on the molecular weight and seems to be a function of the largest molecular dimension. The scattering diagrams apparently show that the average stacking distance between the rigid core is the same in both cases.

In this case, we must emphasize that the rigid imine first central linkage appears to be more favourable to induce a columnar phase than nematic and smectic C phases. Moreover, the molecular arrangement proposed in [4] seems to be unrealistic here. As a consequence of the presence of the two imines, the terminal phenyl groups cannot be easily bent: the passage from the trans to the cis imine isomer involves too high an energy. This observation is also verified if we compare the series IIA with the isomeric series [3]:
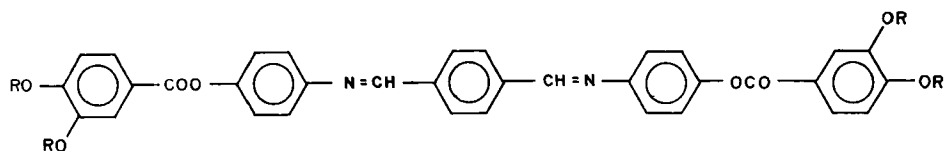
In this, the first central linkage (-COO-) is flexible, the nematic phase is observed in three compounds (n = 6–8) and the smectic C is present in nearly all derivatives
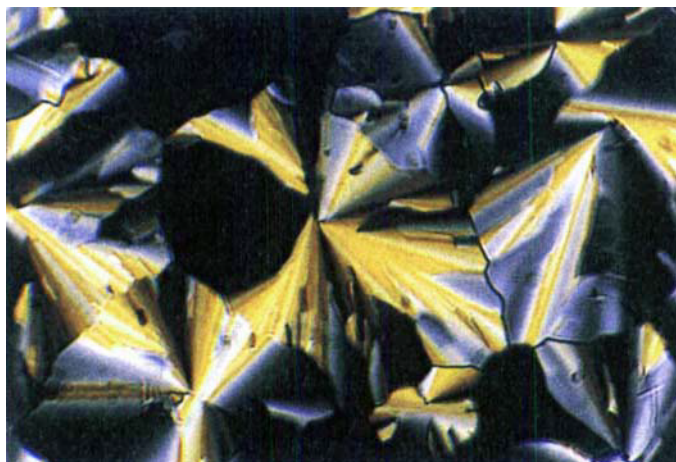
Figure 4.   Optical textures of hexagonal columnar phase IB ($n = 12$) at 150°C.
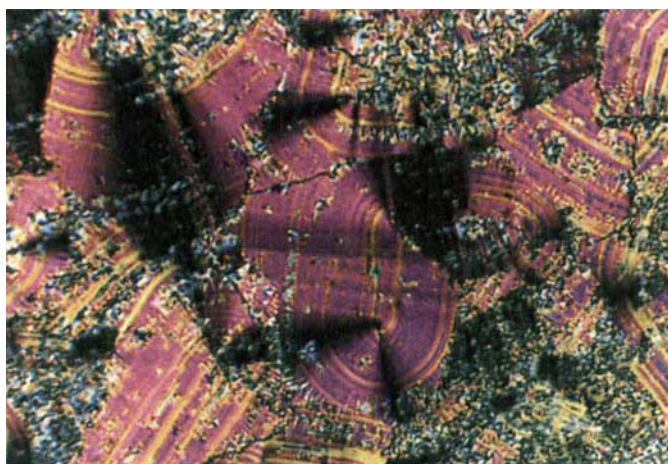
Figure 6.   Optical textures of the unknown columnar phase, IIA ($n = 10$) at 160°C.

($n = 6$–12) except $n = 14$ (see figure 5). This behaviour is still present in the next series.

Series IIB (see figure 7 and table 4)

This series with the more rigid linkage and the flexible cyclohexyl ring, also does not exhibit the nematic phase but the smectic C phase appears from $n = 7$ to $n = 11$. The more interesting behaviour in this series is the existence of the cubic phase [2]. This uncommon phase is found in a few series:

$R = n\text{-}C_{16}H_{33}\text{-};\ n\text{-}C_{18}H_{37}\text{-};\ X = -NO_2$ [7]
$X = -CN$ [8]
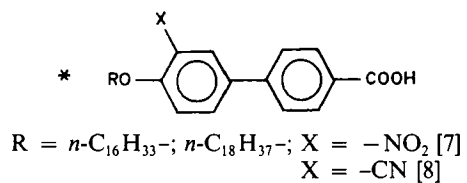
Figure 5. A plot of the transition temperatures against n, the number of carbon atoms in the alkoxy chain of IIA.

$$* \quad RO \!-\!\!\bigcirc\!\!-\! CO\!-\!NH\!-\!NH\!-\!CO \!-\!\!\bigcirc\!\!-\! OR \quad [9]$$

$$R = n\text{-}C_{10}H_{21}-$$
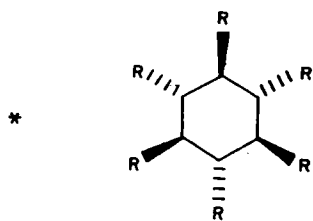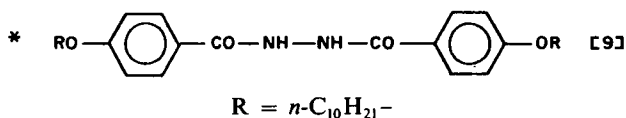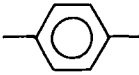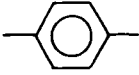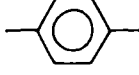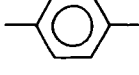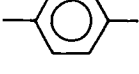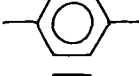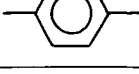
$$R = n\text{-}C_4H_9\text{-}COO\text{-} \ [10]$$

$$R = n\text{-}C_{14}H_{29}\text{-}COO\text{-} \ [11]$$

Billard showed that the cubic phases in the four last series are not miscible [11]. Let us come back to our series. The cubic phase is observed in three compounds, the

Table 3.   The transition temperatures (°C) and enthalpies (kJ mol^{-1}) of compounds IIA.

—⟨A⟩—	n	C		S$_C$		$\phi_?$		ϕ_h		I
—⟨O⟩—	7	●	166 62·03	—	186 5·68	—		—		●
—⟨O⟩—	8	●	159·3 66·61	●	180 5·59	—		—		●
—⟨O⟩—	9	●	157·7 70·98	●	172 4·91	—		—		●
—⟨O⟩—	10	●	153 74·96	—		●	162 3·10	●	172 2·76	●
—⟨O⟩—	11	●	153 87·53	—		●	155·5 2·89	●	173 3·25	●
—⟨O⟩—	12	●	149 87·44	—		—		●	170 3·40	●
—⟨O⟩—	13	●	147 94·75	—		—		●	168 3·29	●
—⟨O⟩—	14	●	146 108·39	—		—		●	168 4·25	●

transition temperatures of which are different on heating and on cooling (see table 4). This behaviour is also found for the 4-alkoxy-3-nitrobiphenyl carboxylic acids [12]. The hexagonal columnar phase which appears before the cubic phase, on cooling from the isotropic phase, might have a lattice with a parameter more than twice the molecular length. For example, with $n = 11$, the parameter of the hexagonal lattice a is 135 Å while the length of the molecule is about 63 Å. This is the most striking difference between a hexagonal columnar phase above the cubic phase with a normal hexagonal columnar phase for biforked mesogens for which the lattice constants vary from 45 Å to 49 Å following the length of the paraffinic chain. Recently this cubic phase was also found in several new biforked mesogens derived from 3(3,4-dialkoxyphenyl)-propanoic acids [16, 17].

3.2.   Calorimetric studies

All of these biforked mesogens have rather large melting enthalpies (from 33 to 127 kJ mol^{-1}). Moreover they do not display a large supercooling (in most cases, the mesophase crystallizes 10°C below the melting point). As the melting temperatures and enthalpies of biforked mesogens are not too different a eutectic mixture of two tretracatenars does not decrease too much the melting temperature. So it is difficult to obtain biforked mesogens with low transition temperatures, except in two
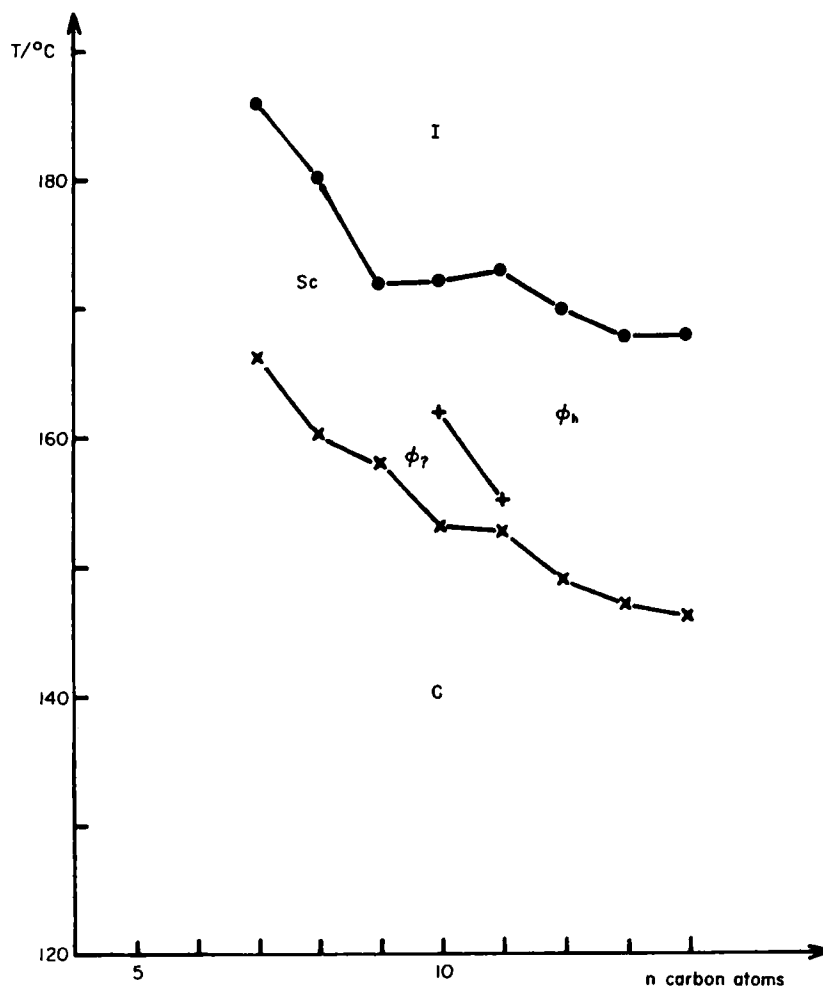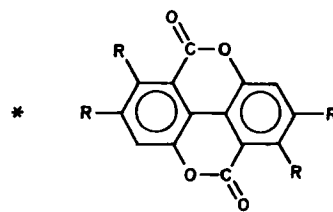
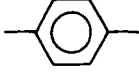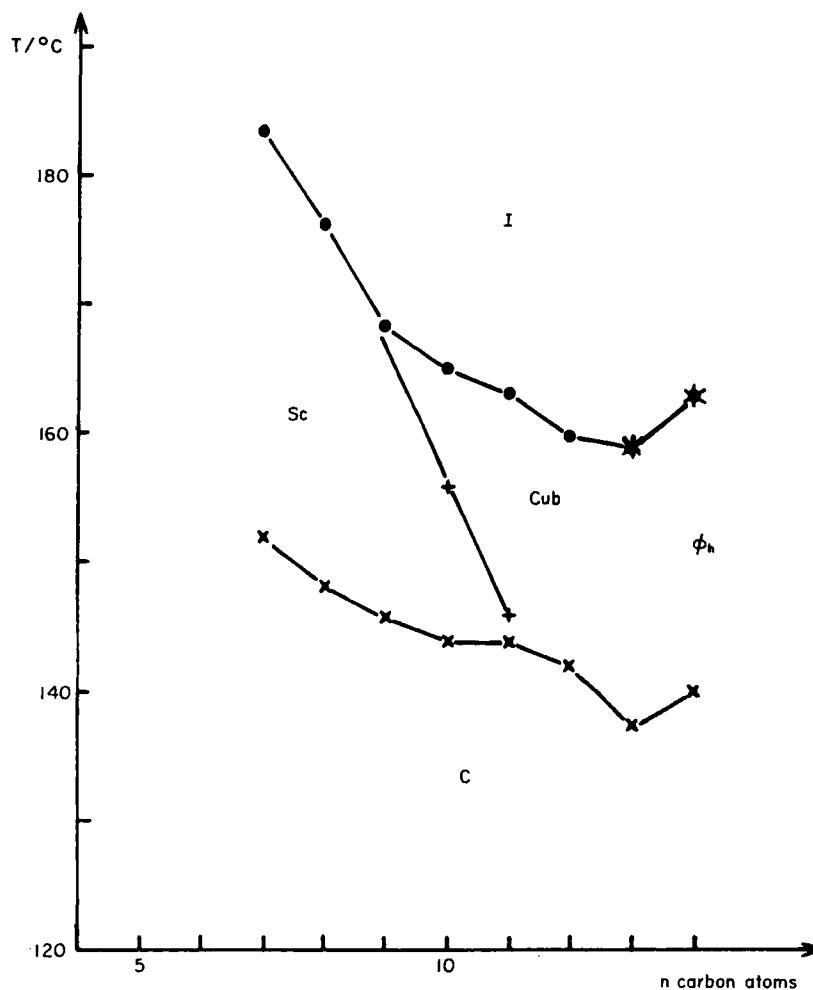Figure 7. A plot of the transition temperatures against n, the number of carbon atoms in the alkoxy chain of IIB.

cases:

biforked compounds subsituted in meta, meta positions [3]. In this case we obtain only columnar phases and there is no competition between lamellar and columnar ordering,

compounds with polyethylenoxy chains [13] instead of aliphatic substituents.
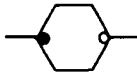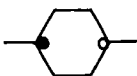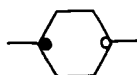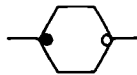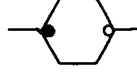
Now, let us point out some interesting facts about the transition enthalpies of the different mesophases:

the N–I transition enthalpy is around $1 \, kJ \, mol^{-1}$,

the S_C–N or S_C–I transition enthalpy varies between 5 and $8 \, kJ \, mol^{-1}$ but that for S_C–Cub or S_C–ϕ_h transition is about $2 \cdot 5 \, kJ \, mol^{-1}$,

in almost all cases, the sum of the transition enthalpies between the S_C, Cub and ϕ_h phases to isotropic is approximately $6 \, kJ \, mol^{-1}$.

Table 4. The transition temperatures (°C) and enthalpies (kJ mol^{-1}) of compounds IIB.

(structure)	n	C	S$_C$	Cub	ϕ_h	I
(diagram)	7	• 152	• 183	—	—	•
(diagram)	8	• 148 81·90	• 176 5·73	—	—	•
(diagram)	9	• 146·5 81·25	• 168·5 5·49	—	—	•
(diagram)	10†	• 144 93·47	• 156 2·30	• 165 3·00	—	•
(diagram)	11†	• 144 102·85	• 146 2·42	• 163 3·02	—	•
(diagram)	12†	• 142 106·72	–	• 162 3·04	—	•
(diagram)	13†	• 141 94·13	—	—	— 163 3·83	•
(diagram)	14	• 140 127·74	—	—	• 163 4·27	•

† The transition temperatures of these compounds on cooling are different:

     n = 10   I   157   S$_C$ 138   C

     n = 11   I   158 ϕ_h^{**} 147   Cub   140   S$_C$ 135   C

     n = 12   I   160 ϕ_h^{**} 138   C

‡ This hexagonal columnar phase has a large lattice spacing.

4. Conclusion

In these four new series of biforked mesogens, nematic smectic C, hexagonal, rectangular, unknown columnar and cubic phases have been found and characterized. These results confirm the rich mesomorphic behaviour of this five ring system with four chains in the meta and para positions. In spite of the rigidity of the end imine linkages (series IIA,B) the hexagonal columnar phase is more favoured than in the series IA,B with the more flexible end ester linkages. We must underline some interesting features:

the nematic phase is observed only in series IA,B with the first ester linkage,

the cubic–hexagonal phase transition only occurs on cooling and depends on the rate of cooling,

the transformation cubic–S$_C$ is not very clear. It is interesting to continue to work on other systems.

5. Experimental

The infrared spectra were recorded using a Perkin–Elmer 783 spectrophotometer and the NMR spectra with a Bruker 270 MHz. The microanalysis were performed by C.N.R.S. Laboratory 'Service Central d'Analyse'.

General procedure for the preparation of 3,4-dialkoxybenzaldehydes: 3,4-dihydroxybenzaldehyde (6·9 g, 50 mmol) and alkylbromide (110 mmol) were dissolved in DMF (200 ml). Potassium carbonate (50 g, 360 mmol) was added and the mixture was refluxed for 6 hours. The mixture was cooled, diluted with water and extracted twice with ether. The combined ethereal layers were washed twice with water and once with brine. The organic solution was then dried over sodium sulphate. Evaporation and chromatography on silica gel with a hexane–ether (80–20) mixture furnished 3,4-dialkoxybenzaldehydes as white crystals in 70–75 per cent yields (recrystallized in absolute ethanol).

The melting points for the complete series with alkyl tails C_7 to C_{14} are:

C_n	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
m.p./°C	48	55	62	65	69	71	76	78

General procedure for the preparation of 3,4-dialkoxybenzoic acids: Ethyl 3,4-dihydroxybenzoate (9·1 g, 50 mmol), was added to a solution of (6·2 g, 110 mmol) of KOH in a 200 ml ethanol–water (4:1) mixture. To this hot solution, alkyl bromide (110 mmol) was added dropwise, and the mixture was refluxed for 4 hours. After cooling, it was saponified with a solution of 10 g of KOH in 10 ml water. The resulting mixture was then refluxed for 2 hours and cooled to room temperature. The solvent was evaporated and the mixture was acidified with concentrated hydrochloric acid and crushed ice. The product was filtered off, washed with water and recrystallized in absolute ethanol. Yield: 48–71 per cent (white crystals).

The melting points for the complete series with alkyl tails C_6 through C_{14} are:

C_n	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
m.p./°C	128	127	125	124	123	123	121	120	119

General procedure for the preparation of 3,4-dialkoxybenzylidene 4-hydroxyaniline: 3,4-dialkoxybenzaldehyde (20 mmol) and 4-aminophenol (2·2 g, 20 mmol) were dissolved in ethanol (50 ml) with two drops of acetic acid as catalyst. The mixture was refluxed for 2 hours. After cooling in a refrigerator, the product recrystallized as slightly yellow crystals in 57–79 per cent yield.

The melting points for the complete series with alkyl tails C_7 through C_{14} are

C_n	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
m.p./°C	98	99	103	103	107	108	108	109

General procedure for the preparation of 4-benzyloxyphenyl 3,4-dialkoxybenzoates: 3,4-dialkoxybenzoyl chloride (prepared from the corresponding acid and an excess of thionyl chloride (25 mmol) was dissolved in dry pyridine (50 ml). 4-benzyloxyphenol (5 g, 25 mmol) was added and the mixture was stirred at room temperature for

20 hours and then poured into crushed ice/concentrated sulphuric acid. The compounds were filtered off and washed with water. Recrystallization from ethyl acetate furnished the products as white crystals in 59–84 per cent yields.

The melting points for the complete series with alkyl tails C_6 through C_{14} are:

C_n	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
m.p./°C	86	96	82	84	86	84	87	83	92

General procedure for the preparation of 4-hydroxyphenyl 3,4-dialkoxybenzoates: 4-benzyloxyphenyl 3,4-dialkoxybenzoates (20 mmol) was dissolved in acetic acid (150 ml) and THF(50 ml). Palladium on charcoal (1·5 g, 10 per cent) was added and the mixture was stirred under hydrogen. After filtration the solvent was evaporated and the product was recrystallized from hexane–toluene (9 : 1) mixture affording the products as white crystals in 64–90 per cent yields.

The melting points for the complete series with alkyl tails C_6 through C_{14} are:

C_n	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
m.p./°C	108	104	96	95	97	101	98	98	96

General procedure for the preparation of series IA compounds: 4-hydroxyphenyl 3,4-dialkoxybenzoate (2·2 mmol), terephthalic acid (0·166 g, 1 mmol), dicyclohexyl-carbodimide (DCC) (0·21 g, 1 mmol) 4-dimethylaminopyridine (DMAP) (20 mg) were added in CH_2Cl_2 (30 ml). The mixture was stirred at room temperature for 20 hours. After filtration the filtrate was evaporated and the residue was chromatographed on silica gel with a toluene–dichloromethane (4 : 1) mixture. The desired derivative was recrystallized in a ethanol–toluene (1 : 1) mixture. Yield 30–57 per cent.

IR (Nujol, cm^{-1}): 1740, 1720, 1595, 1510, 1250, 820

^{1}H-NMR (CDCl$_3$, δ): 8·32 (s, 4 H), 6·90–7·84 (m, 6 H) 7·28 (s, 8 H),
  4·02–4·09 (m, 8 H, 4-CH$_2$O), 1·81–1·85 (m, 8 H),
  1·25–1·54 (m, 24–84 H), 0·84–0·88 (m, 12 H)

Anal. Calcd for IA (n = 10); $C_{74}H_{102}O_{12}$: C, 75·13; H, 8·63
  Found   : C, 75·04; H, 8·41

The compounds of series IB were prepared and purified as we have described.

The compounds of series IIA and IIB were prepared in a similar fashion but they were purified by recrystallization in an ethanol–toluene (1 : 1) mixture (three times).

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