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PRELIMINARY COMMUNICATIONS

A new series of polar fluorodibenzoates with various smectic modifications†

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Four series of 4-alkoxyphenyl 4″-(4′-cyano- or nitro-benzoyloxy)-2″- or -3″-fluorobenzoates have been synthesized and the corresponding mesophases identified. These series show a rich variety of smectic modifications including several kinds of smectic C phases. A comparison of these series with related strongly polar mesogens is given.

We have continued our investigations on strongly polar mesogenic systems with the synthesis of four series of 4-alkoxyphenyl 4″-(4′-cyano-or nitro-benzoyloxy)-2″-or-3″-fluorobenzoates which derive from the general formulae shown in figure 1.

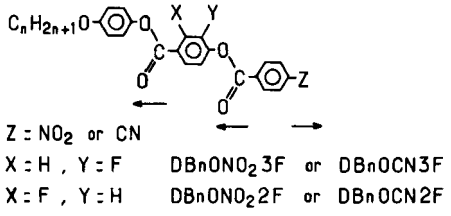
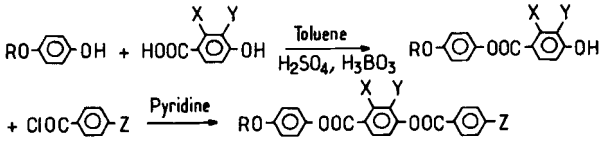


Figure 1. Structural formulae and acronyms of the various series synthesized. The arrows indicate the relative longitudinal dipole moments of the two ester linkages and of the terminal cyano or nitro group.

The series have a molecular structure basically similar to that of the well-known dibenzoate series (DBn) [1–3] and of their chlorinated homologues [4, 5]. The purpose of this work was to check the influence of the lateral halogen substituent with its lateral dipole moment and steric hindrance on the mesomorphic polymorphism in comparison with the unsubstituted [1–3], or methylated compounds [6].

The four series were synthesized following the same scheme:



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The starting 2- or 3-fluoro-4-hydroxybenzoic acids were prepared following Gray *et al.* [7] from commercial 2- or 3-fluorophenol. All of the final products gave single spots by thin layer chromatography. Transition temperatures were measured using a polarizing microscope fitted with a Mettler FP5 heating stage. The identification of the various mesophases was performed by comparison with similar series [1–4], texture observations and finally, when necessary, by the contact method.

The transition temperatures of the fluorinated dibenzoate derivatives are given in table 1 (DBnOCN3F), table 2 ($DBnONO_2$3F), table 3 (DBnOCN2F) and table 4 ($DBnONO_2$2F). In table 5 we give a comparison of a few typical derivatives of the unsubstituted [1] fluorinated and chlorinated [4] dibenzoates series.

Table 1. Transition temperatures (°C) of the DBnOCN3F.

R	K		S_{C_2}		$S_{\tilde{C}}$		S_C		S_A		N		I
C_7H_{15}	●	101		—	●	105		—	●	109	●	224·5	●
C_8H_{17}	●	101	●	(84)	●	112·5		—	●	140	●	218	●
C_9H_{19}	●	99	●	109·3	●	110·4	●	111·7	●	177	●	212	●
$C_{10}H_{21}$	●	100·5	●	118		—		—	●	192	●	207	●
$C_{11}H_{23}$	●	98·5	●	121·5		—		—	●	199	●	204	●
$C_{12}H_{25}$	●	102	●	123		—		—	●	201	●	201·5	●

$S_{\tilde{C}}$ smectic C phase with a ribbon structure [8].
( ) denotes a monotropic transition in all the tables 1 to 5.

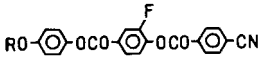

Table 2. Transition temperatures (°C) of the $DBnONO_2$3F compounds.

R	K		S_A		N_{re}		S_A		N		I
C_7H_{15}	●	112	●	(87·5)		—		—	●	206·5	●
C_8H_{17}	●	97	●	(91)		—		—	●	203	●
C_9H_{19}	●	99	●	(87)	●	134	●	170	●	199	●
$C_{10}H_{21}$	●	111	●	(82)	●	(98)	●	188	●	199	●
$C_{11}H_{23}$	●	112		—		—	●	194	●	195	●

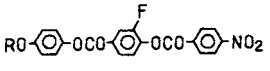

Table 3. Transition temperatures (°C) of the DBnOCN2F compounds.

R	K		$S_{C?}$		S_{C_2}		S_A		N		I
C_8H_{17}	●	106	●	(105)	●	131	●	199	●	228	●
C_9H_{19}	●	95	●	99·5	●	133	●	207	●	223	●
$C_{10}H_{21}$	●	103·5		—	●	139	●	216·5	●	222	●
$C_{11}H_{23}$	●	99		—	●	141	●	213·5	●	215	●

$S_{C?}$ biaxial bilayered fluid mesophase.
S_{C_2} bilayer smectic C phase.

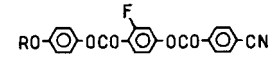

Table 4. Transition temperatures (°C) of the $DBnONO_2 2F$ compounds.

R	K		S_C		S_{A_2}		S_{A_d}		N		I
C_7H_{15}	●	97·5		—		—	●	124	●	214	●
C_8H_{17}	●	95·5		—	●	127	●	129·5	●	214	●
C_9H_{19}	●	96		—	●	129	●	142·8	●	210·5	●
$C_{10}H_{21}$	●	95·5		—	●	130·8	●	198	●	209·2	●
$C_{11}H_{23}$	●	97		—	●	131	●	204·5	●	206·5	●
$C_{12}H_{25}$	●	95·5	●	(94)	●	131	●	206·5		—	●

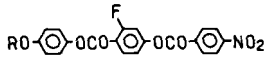

Table 5. Some typical mesomorphic sequences and transition temperatures (°C) in cyano- and nitro-alkoxybenzoate series ($DBnONO_2$, DBnOCN) and in their corresponding 2″- or 3″-halogeno substituted homologues.

$DB9ONO_2$	K	109	(S_{C_2}	96)	$S_{\tilde{C}}$	118	S_{A_1}	124	N_{re}	127	S_{A_d}	138				
							N_{re}	156	S_{A_d}	195	N	224	I			
$DB9ONO_2 3F$	K	99	(S_A	87)	N_{re}	134	S_A	170	N	199	I					
$DB10ONO_2 3Cl$	K	80	($S_{\tilde{C}}$	67·5)	(S_A	68)	N_{re}	102·5	S_A	140	N	170	I			
$DB10ONO_2 2Cl$	K	150	S_{A_2}	110	S_{A_d}	152	N	163	I							
$DB9ONO_2 2F$	K	96	S_{A2}	129	S_{A_d}	143	N	210·5	I							
DB7OCN	K	130·5	S_{A_2}	174	S_{A_d}	181	N	246	I							
DB9OCN	K	132	(S_C	111)	S_{A_d}	213	N	232	I							
DB9OCN2F	K	95	$S_{C?}$	99·5	S_{C_2}	133	S_A	207	N	223	I					
DB9OCN2Cl	K	100	$S_{C?}$	106	S_{C_2}	121	S_A	173	N	182	I					
DB10OCN3Cl	K	118	(S_C	106)	S_A	160	N	183	I							
DB9OCN3F	K	99	S_{C_2}	109·3	$S_{\tilde{C}}$	110·4	S_C	111	S_A	177	N	212	I			

(1) *DBnOCN3F:* This series is of a special interest concerning smectic C polymorphism (cf. table 1), especially with the nonyloxy derivative. On cooling from the S_A phase a S_C phase becomes visible through a schlieren texture (cf. figure 2(*a*)), then near 110·4°C a sudden textural change corresponds to the $S_{\tilde{C}}$ tilted smectic phase with a ribbon structure [8] (cf. figure 2(*b*)) and finally this texture transforms at 109·3°C to give again a typical S_C schlieren texture. This peculiar behaviour was also revealed in another polar series [9], and will require further physical investigations. Finally we must emphasize that this cyanodibenzoate series does not exhibit re-entrant nematic phases, and this behaviour confirms, as was recently reported [9], that when the longitudinal dipole moments of *X* and *Y* (cf. figure 1) are opposed to that of the *Z* terminal group, the cyano derivatives are devoid of any re-entrant nematic phase. On the other hand the nitro-derivatives are more favourable in showing such behaviour [1, 4, 9].

(2) *$DBnONO_2 3F$:* This series (cf. table 2) provides examples of re-entrant nematic phases ($R = C_9H_{19}$, $R = C_{10}H_{21}$) with low temperature monotropic S_A phases.

(3) *DBnOCN2F:* This series gives another example of the new, unknown smectic C phase $S_{C?}$ [10] (cf. table 3), moreover, this phase is enantiotropic in the nonoloxy

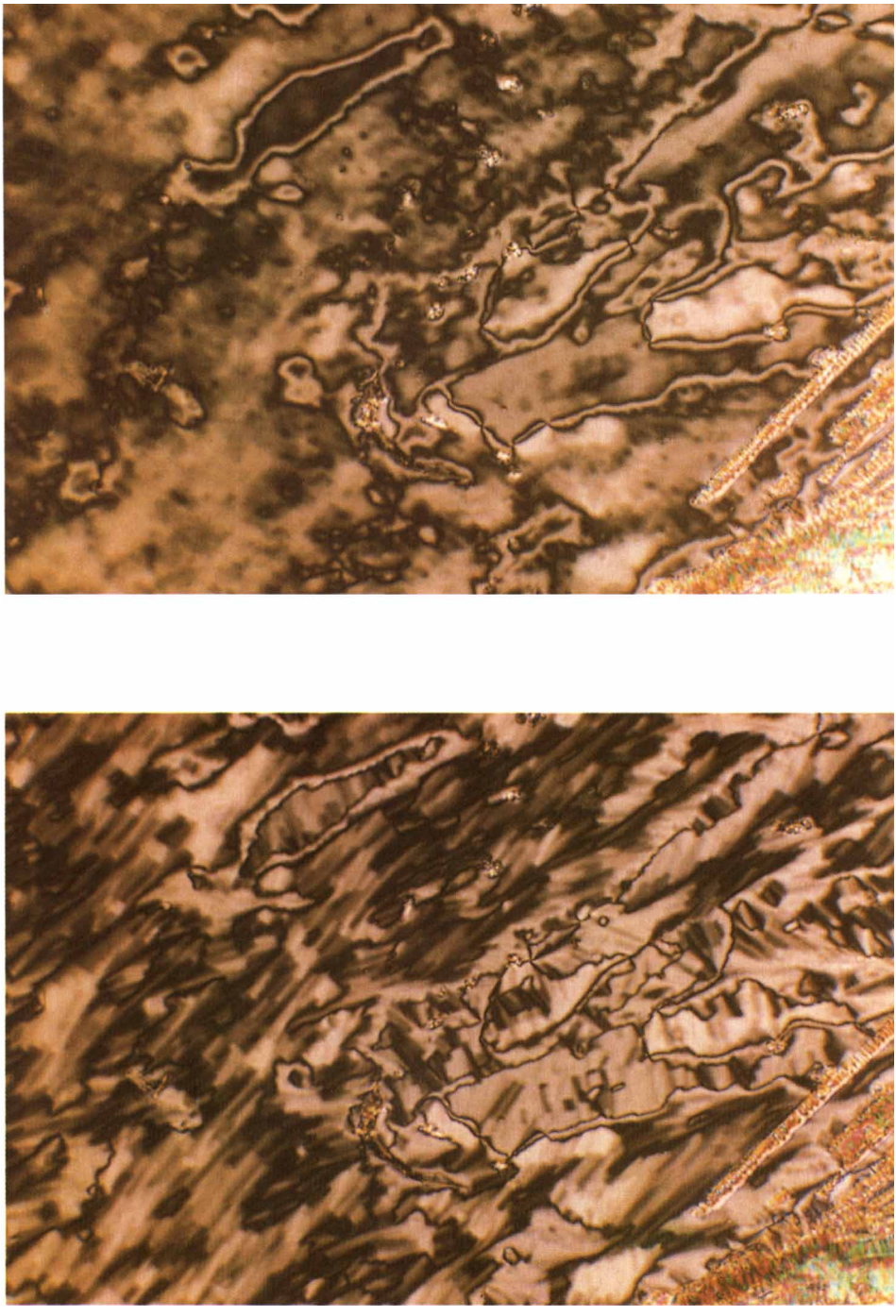

Figure 2. Optical textures of DBnOCN3F between crossed polarizers: (*a*) 110·8°C S_C phase, (*b*) 109·4°C S_C phase (same area).

derivative with the sequence:

$$K\text{–}S_{C?}\text{–}S_{C_2}\text{–}S_A\text{–}N\text{–}I.$$

This confirms, to some extent, that the new phase is associated with the presence of a strongly polar lateral substituent such as fluorine or chlorine [4, 5] and will stimulate investigations by means of dielectric measurements [11, 12].

(4) *DBnONO$_2$2F:* This last series (cf. table 4) offers a new example of a S_{A_2}–S_{A_d} [4, 13, 15] transition directly observable by optical microscopy. This phenomenon corresponds to a straightforward enhancement of the layer spacing and to a rather strong heat of transition [4, 13, 15].

In table 5 we have summarized some typical data concerning unsubstituted alkoxydibenzoate compounds (cyano and nitro) and their corresponding 2 or 3 substituted fluoro or chloro derivatives. Several comments can be made.

There is a clear connection between the depression of the clearing temperature and the steric hindrance of the lateral substituent: $H < F \ll Cl$.

Surprisingly [14] the presence of these lateral halogen substituents in either the 2 or 3 positions does not cause a strong reduction in the thermal stability of the smectic phases.

Once more when the longitudinal dipole moment of the lateral halogen substituent is parallel to that of the nitro group (3-position) it enhances the re-entrant phenomenon.

Two aspects of mesomorphic behaviour are clearly connected with the presence of the lateral halogens: the existence of the S_{A_2}–S_{A_d} transition directly visible by optical microscopy (DBnONO$_2$2F and DBnONO$_2$2Cl) and the existence of the new $S_{C?}$ phase (DBnOCN2F and DBnOCN2Cl).

Apart from these peculiar effects it is rather difficult to find a close relationship between the molecular structure and the polymorphism. However these series provide interesting mesomorphic materials and will probably stimulate more physical investigations.

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