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Liquid Crystals

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Properties of the liquid crystals formed by certain 4'-*n*-alkylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates

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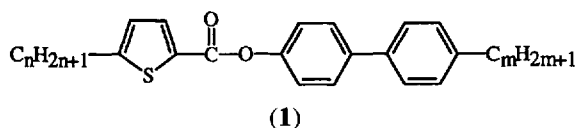
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Thirty compounds, ten members of each of three homologous series of esters derived from 4-hydroxy-4'-*n*-octyl-, -nonyl-, and -decyl-biphenyl and the 5-*n*-alkylthiophene-2-carboxylic acids (methyl through to decyl homologues) have been prepared. The liquid crystal properties of these esters, which show extensive smectic polymorphism, have been investigated by thermal optical microscopy, differential scanning calorimetry, and miscibility studies. Four members of the corresponding 4-*n*-alkylbenzoates have also been prepared in order to compare their liquid crystal behaviour with the 5-*n*-alkylthiophene-2-carboxylate counterparts: both smectic and nematic thermal stability are higher for the 4-*n*-alkylbenzoates, by 30.6° and 36.8°C, respectively.

1. Introduction

As a continuation of our study [1-3] of the liquid crystal behaviour of three-ring esters containing a thiophene ring we have now prepared and investigated the mesomorphic properties of ten members of each of three homologous series of 4'-*n*-alkylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (**1**: $m = 8, 9,$ and 10 ; $n = 1-10$). Certain closely related esters have been cited in patents, namely, $m = 5$ [4]; $n = 3$ and $m = 8$ [5] and 10 [6]; $n = 12$, but no systematic study of homologation in these esters, which show extensive smectic polymorphism, has previously been undertaken, nor has a comparison of mesophase thermal stability with the analogous 4-*n*-alkylbenzoates which are also cited in a patent [7]. The compounds have been investigated by optical microscopy, differential scanning calorimetry, and miscibility studies.



2. Results and discussion

Ten members of each homologous series, 4'-*n*-octyl-, -nonyl-, and -decyl-biphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (**1**: $m = 8, 9, 10$; $n = 1-10$) have been prepared. The mesophase transition temperatures of these compounds were determined by optical microscopy and confirmed by differential scanning calorimetry. Assign-

ments of phase type were made by microscopic observation of the optical textures obtained on cooling from the isotropic liquid and by miscibility studies using compounds of established phase types as standard materials.

The transition temperatures for the members of the three homologous series are listed in tables 1, 2, and 3 and plotted against n , the number of carbon atoms in the alkyl group of the thiophene moiety, in figures 1, 2, and 3.

The liquid crystal behaviour of the three homologous series, which show extensive smectic polymorphism, is closely similar. A detailed account of the mesomorphic properties of the decyl homologues ($m = 10$; $n = 1-10$) is given in the following discussion and is followed by an outline treatment of the corresponding octyl and nonyl homologues ($m = 8, 9$; $n = 1-10$).

2.1. 4'-*n*-Decylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (**1**: $m = 10$; $n = 1-10$)

It is convenient to discuss the form of the transition temperature plot (see figure 1) at the outset before considering the assignments of phase type by optical texture observations and miscibility studies.

All ten members give an enantiotropic nematic mesophase and the points for the N-I transition temperatures show the expected alternation (see figure 1) and fit two curves which initially fall smoothly as n increases, with the odd n curve uppermost, before revealing an upturn then convergence and levelling off in the region $n = 6-9$ and finally congruence at $n = 10$ with the point for the S_C-I transition temperature of this homologue. The smectic behaviour of the series comprises two distinct

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Table 1. Transition temperatures (°C) for the 4'-*n*-decylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates.

<i>n</i>	Cr-N	N-I	S _C -I	S _C -N	S _I -N	CrG-N	S _I -S _C	S _F -S _I	CrJ-S _F	CrK-CrJ	N-Cr
1	102.6	120.1									70.2 <u>CrG-Cr</u>
2	72.0	109.7				(66.4)					40.0
3	83.0	110.8				(74.1)					72.2 <u>CrK-Cr</u>
4	Cr-K 70.0	103.7			82.7			81.5	80.5	79.5	35.0
5	73.2	106.7		87.7			86.3	84.3	82.5	79.5	35.0
6	67.4 <u>Cr-CrJ</u>	103.8		92.8			88.0	85.0	80.9	79.0	45.5
7	76.8 <u>Cr-S_F</u>	106.7		97.0			86.5	83.4	78.1	(75.6)	50.4
8	75.8	107.0		102.5			86.7	83.9	(74.0)	(66.1)	47.5
9	79.5	106.3		104.6			83.0	80.6	(67.9)	(55.1)	52.0 <u>CrJ-Cr</u>
10	77.0		106.5				81.9	79.9	(59.4)		45.0

Symbols have their usual meaning: Cr, crystal; N, nematic; S_A, smectic A; CrJ, crystal J; I, isotropic liquid, etc. Thus, Cr-N indicates the temperature (m.p.) at which the crystal (Cr) melts to the nematic phase (N).

Temperature of crystallization (at a cooling rate of approximately 3°C min⁻¹).

Values in parentheses are for monotropic transitions.

Table 2. Transition temperatures (°C) for the 4'-*n*-nonylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates.

<i>n</i>	Cr-N	N-I	S _C -N	CrG-N	S _I -S _C	S _F -S _I	CrJ-S _F	CrK-CrJ	N-Cr
1	112.4	122.5							71.5 <u>CrG-Cr</u>
2	89.7	114.6		(65.0)					55.3
3	88.2 <u>Cr-CrG</u>	113.3		(76.7)					55.5
4	71.1	106.6		81.6					35.0
5	80.0 <u>Cr-CrK</u>	110.2		85.8					45.5 <u>CrK-Cr</u>
6	74.5 <u>Cr-S_I</u>	107.2	91.4		88.3	87.0	85.4	82.6	58.5
7	86.3 <u>Cr-S_C</u>	110.2	98.0		86.4	(84.8)	(82.2)	(79.0)	62.8
8	88.8	108.1	100.6		(84.9)	82.6	(76.4)	(68.0)	66.0 <u>CrJ-Cr</u>
9	84.8 <u>Cr-S_F</u>	109.3	104.4		(82.2)	(78.8)	(70.9)		61.0
10	75.0	107.0	104.9		80.5	77.9	(63.4)		62.9

Symbols have their usual meaning: Cr, crystal; N, nematic; S_A, smectic A; CrJ, crystal J; I, isotropic liquid, etc. Thus, Cr-N indicates the temperature (m.p.) at which the crystal (Cr) melts to the nematic phase (N).

Temperature of crystallization (at a cooling rate of approximately 3°C min⁻¹).

Values in parentheses are for monotropic transitions.

sections. The homologues *n* = 2 and 3 give only a monotropic crystal G phase on cooling the nematic phase, contrasting with the properties of the higher members. Thus, on cooling, the homologue *n* = 4 gives first an S_C phase, then an S_F phase, and finally crystal J and K phases. The homologues *n* = 5–9 reveal the same phase sequence, except that an additional S_I phase is interposed between the S_C and S_F phases, and a similar phase sequence is shown by the member *n* = 10, although crystallization occurs in

the J phase before transition to the K phase takes place. The points for the S_C-S_I and the S_I-S_F transition temperatures alternate and lie on two curves which reveal a very shallow rise then a fall as *n* increases, with the even *n* curve uppermost. These curves are shown in figure 1 as hatched regions, both for clarity and to indicate the extent of the alternation of the S_C-S_I and S_I-S_F transition temperatures.

The crystal G phase of the homologues *n* = 2 and 3

Table 3. Transition temperatures (°C) for the 4'-*n*-octylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates.

<i>n</i>	Cr-N	N-I	S _C -N	CrG-N	S _I -S _C	CrJ-S _I	CrK-CrJ	N-Cr
1	107.0	120.5						67.9
2	91.8	112.3						68.3
3	88.9	110.8		(73.6)				<u>CrG-Cr</u> 57.0
4	90.0	104.6		(79.0)				50.0
5	82.4	108.4		(82.3)				55.6
6	<u>Cr-CrK</u> 78.0	104.5	86.7		85.0	82.2	80.7	<u>CrK-Cr</u> 58.4
7	<u>Cr-S_C</u> 88.0	107.5	91.6		(81.6)	(78.0)	(68.0)	66.0
8	87.3	106.5	96.3		(80.0)	(71.1)		<u>CrJ-Cr</u> 70.2
9	81.4	106.0	98.8		(75.4)	(63.2)		63.2
10	<u>Cr-S_I</u> 72.5	105.3	101.0		73.0			<u>S_I-Cr</u> 47.9

Symbols have their usual meaning: Cr, crystal; N, nematic; S_A, smectic A; CrJ, crystal J; I, isotropic liquid, etc. Thus, Cr-N indicates the temperature (m.p.) at which the crystal (Cr) melts to the nematic phase (N).

Temperature of crystallization (at a cooling rate of approximately 3°C min⁻¹).

Values in parentheses are for monotropic transitions.

separates from the schlieren texture of the nematic phase via dendrites which coalesce to give a mosaic texture characterized by some rather larger angular mosaic areas, many of which develop fine parallel striations as the phase develops with a decrease in temperature and also on standing. In contrast, the homologous *n* = 4-9 give the focal-conic fan and schlieren textures of the S_C phase (also obtained directly via bâtonnets from the isotropic liquid for *n* = 10). The S_C focal-conic fans have a much smoother, less lined appearance than the broken fans of an S_C phase which forms on cooling an S_A phase. For the homologue *n* = 4, the focal-conic fans are particularly clear and well defined and the schlieren texture of the nematic phase changes immediately to a very well-developed S_C schlieren at the N-S_C transition. On cooling the S_C phase of the homologues *n* = 5-10, the focal-conic fans become much more well defined at the transition to the S_I phase and a change of the schlieren into the very characteristic non-focusable, schlieren texture of the S_I phase occurs. At the S_I-S_F transition there is no detectable change in the appearance of the focal-conic fans, but the optical discontinuities of the S_I schlieren texture disappear giving the clearer, more focused S_F schlieren-mosaic texture which is crossed with sharper lines of discontinuity around the platelet areas giving the texture almost mosaic-like clarity. The homologue *n* = 4 gives rise to the S_F phase directly from the S_C phase: the focal-conic fans are clear and well defined and the S_C schlieren texture is replaced by the schlieren-mosaic of the S_F phase. On further cooling, the S_F phase of the homologues *n* = 4-10 gives crystal J phase characterized by a mosaic area composed of large, rather ill-defined platelets and a fan texture which is more broken than that of the preceding S_F

phase, the fans being marked by a rectangular patchwork. On further cooling of the crystal J phase of the homologues *n* = 5-9, the onset of the CrJ-CrK transition is characterized by quite spectacular candy-stripping of the previous mosaic areas, and when thin samples are observed, the focal-conic fans also reveal extensive striping. If left for a period of time, the mosaic areas defined by the previous J phase slowly collapse with the formation of a new mosaic system of the K phase containing both square and rectangular shaped areas.

Miscibility studies using terephthalylidene-bis-4-*n*-butylaniline (TBBA) as a standard material confirmed the identity of the crystal G phase in the homologues *n* = 2 and 3. The phase diagram (see figure 4) for the binary mixture of the propyl homologue with TBBA shows the G phase to be continuous across the miscibility diagram of state. Confirmation of the identities of the S_I and S_F phases was achieved by miscibility studies using terephthalylidene-bis-4-*n*-decylaniline (TBDA) as the standard. The phase diagram for the binary mixture of the homologue *n* = 6 with TBDA is shown in figure 5. The S_I and S_F phases reveal continuous miscibility across the phase diagram. Confirmatory evidence for the identities of the crystal J and K phases in the homologues *n* = 5-9 was provided by miscibility studies using *N,N'*-di-(4-*n*-heptyloxybenzylidene)-*p*-phenylenediamine (HEPTOBPD) as a standard. The diagram of state (see figure 6) for the binary mixture of the homologue *n* = 8 and HEPTOBPD shows the J phase to be continuous across the phase diagram. Although crystallization interferes with the continuum of the K phase across the diagram of state, nevertheless, since there is no marked decrease in the CrJ-CrK temperatures between 0 per cent and 40 per cent by weight of

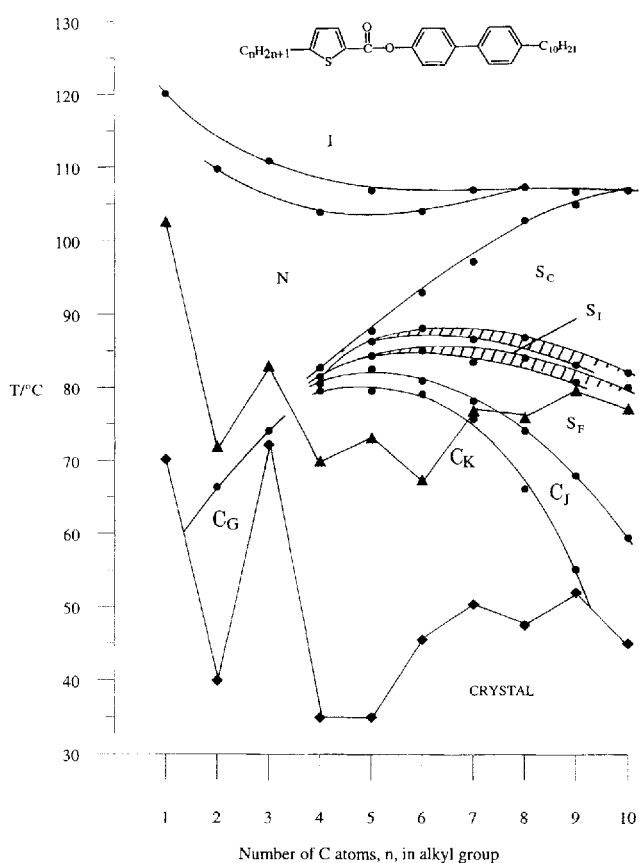


Figure 1. 4'-*n*-Decylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylic acid: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates m.p., (●) mesophase–mesophase transition, and (◆) recrystallization at a cooling rate of approximately 3°C min⁻¹.

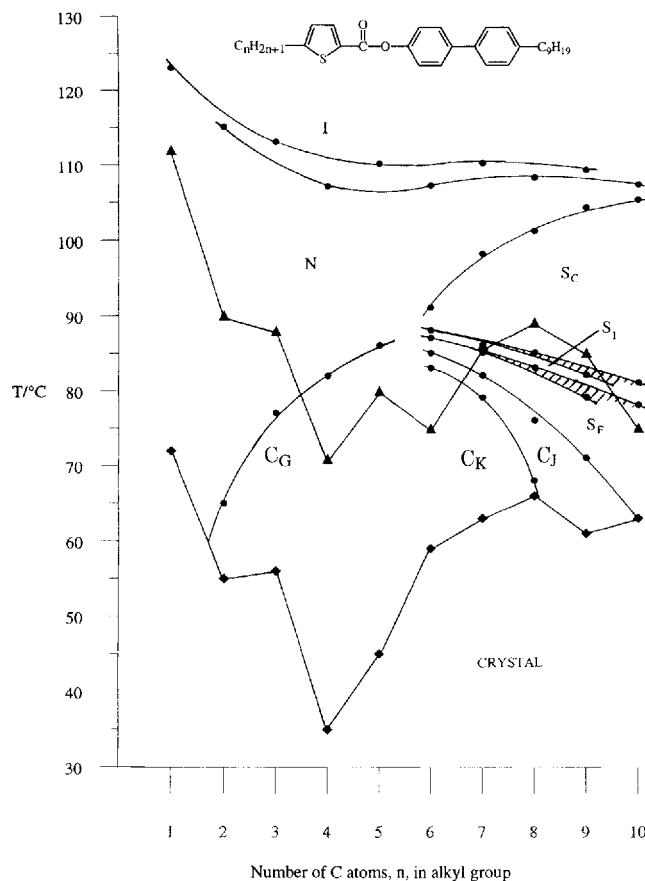


Figure 2. 4'-*n*-Nonylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylic acid: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates m.p., (●) mesophase–mesophase transition, and (◆) recrystallization at a cooling rate of approximately 3°C min⁻¹.

HEPTOBPD this is assumed to be good evidence for the existence of the crystal K phase in the homologue $n = 8$.

The enthalpy data (transition temperatures and transition enthalpies) obtained by differential scanning calorimetry (DSC) for the 4'-*n*-decylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (**1**; $m = 10$; $n = 1$ –10) are listed in table 4. These values (determined at a heating/cooling rate of 10°C m⁻¹) refer to onset temperatures on the second cooling cycle except of crystal–crystal transitions and m.p.s which were recorded on the preceding heating cycle. The transition temperatures are in good agreement with those obtained by thermal optical microscopy although certain transitions (S_I – S_F and CrJ – CrK) associated with a very small enthalpy change were not detected by DSC. Nevertheless, the results clearly support the phase assignments discussed above.

Several crystal–crystal transitions were detected in all the compounds studied. In general, these have very small transition enthalpies and the values have not been included

in table 4, except for the compounds $n = 2$ and 3. These homologues have a Cr–Cr transition associated with a substantial transition enthalpy just prior to the m.p. (the Cr–N transition) which has a very much smaller enthalpy value.

A number of analogous esters, the 4'-*n*-alkylbiphenyl-4-yl 4-*n*-alkylbenzoates (**2**) are cited in a patent [7]. However, transition temperatures for the 4'-*n*-octyl-, -nonyl-, and -decyl-biphenyl-4-yl 4-*n*-alkylbenzoates, corresponding with the 5-*n*-alkylthiophene-2-carboxylates of the present work, are not reported therein, nor does the patent pay much regard to the types of smectic phases shown by the benzoates. Accordingly, we have prepared four homologues (**2**; $m = 10$; $n = 7$ –10) in order to compare the mesophase thermal stability of the 4-*n*-alkylbenzoates with the corresponding 5-*n*-alkylthiophene-2-carboxylates. The transition temperatures of these esters are: *n*-heptyl: S_C –N, 129.4°; N–I, 146.6°; *n*-octyl: S_C –N, 131.8°, N–I, 143.5°, *n*-nonyl: S_C –N, 135.6°; N–I, 142.8°; *n*-decyl: S_C –N, 136.3°; N–I, 140.8°C.

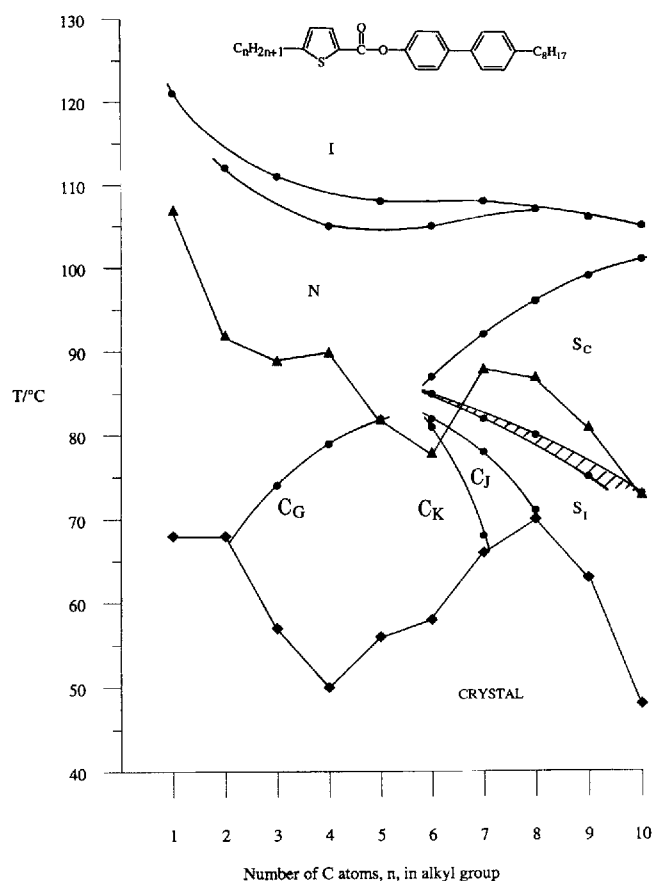
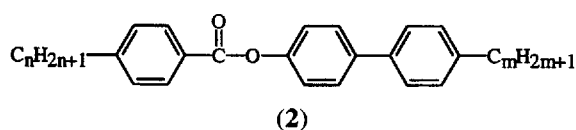


Figure 3. 4'-*n*-nonylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylic acid: transition temperatures against *n*, the number of carbon atoms in the alkyl group. (▲) indicates m.p., (●) mesophase-mesophase transition, and (◆) recrystallization at a cooling rate of approximately 3°C min⁻¹.



Thus, for the members $m = 10$, $n = 7-10$ inclusive, the average nematic (143.4°C) and smectic (133.3°C) mesophase thermal stability of the 4-*n*-alkylbenzoates (2), is greater by 36.8°C and 30.6°C than the corresponding values for the average nematic (106.6°C, assuming T_{N-I} to be the same as T_{S_C-I} for $n = 10$) and smectic (102.7°C) mesophase thermal stability of the 5-*n*-alkylthiophene-2-carboxylates (1). Our study of a very limited number of 4'-*n*-alkylbiphenyl-2-yl 4-*n*-alkylbenzoates (2) has revealed that these esters also show quite extensive smectic polymorphism. We intend to investigate and report on a wider range of the 4-*n*-alkylbenzoates in a future publication.

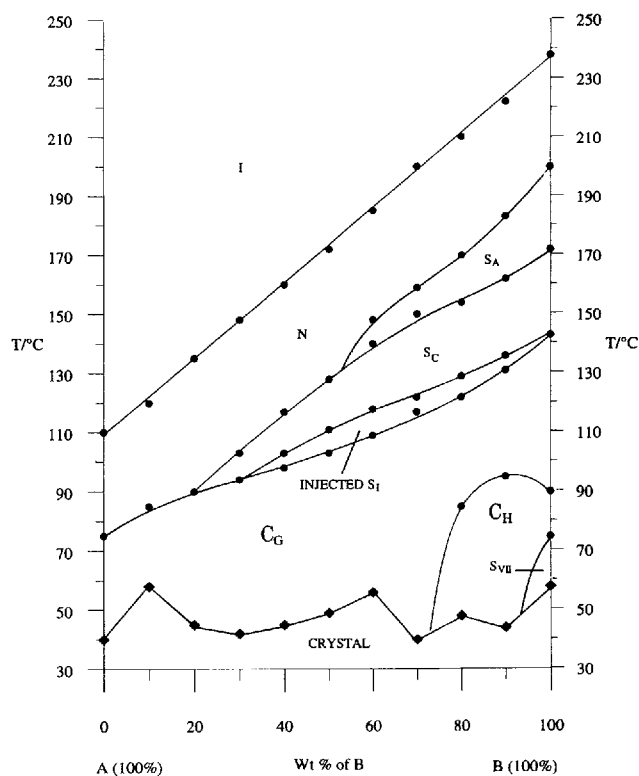


Figure 4. Binary phase diagram for mixtures (wt %) between 4'-*n*-decylbiphenyl-4-yl 5-*n*-propylthiophene-2-carboxylate (A) and TBBA (B). (●) indicates mesophase-mesophase transition and (◆) recrystallization at a cooling rate of approximately 3°C min⁻¹.

2.2. 4'-*n*-Nonylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (1: $m = 9$; $n = 1-10$)

The liquid crystal behaviour of this homologous series is very similar to that of the corresponding decyl homologues discussed above and the transition temperature plot (see figure 2) reveals only minor differences. All ten members show an enantiotropic nematic mesophase and the points for the N-I transition temperatures follow a similar trend to those for the decyl homologues. However, as the homologue $n = 10$ is also nematic, the rising curve for the S_C-N transition temperatures does not meet the falling N-I transition temperature curve. The distinctly different smectic behaviour of the lower and higher members is even more marked in this series than in the decyl homologues. In this instance, for members, $n = 2-5$, show only a crystal G phase ($n = 2$ and 3 being monotropic) and the onset of smectic polymorphism is shifted towards the higher members and commences at $n = 6$. This compound and the subsequent higher homologues exhibit virtually identical smectic properties to their decyl counterparts, the only differences being that, in this instance, the S_C-S_I and S_I-S_F transition temperature curves show a steeper downward trend as the

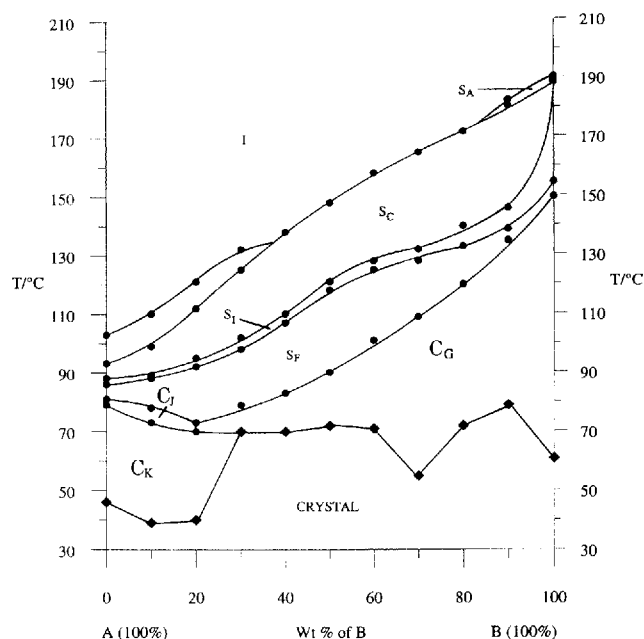


Figure 5. Binary phase diagram for mixtures (wt %) between 4'-*n*-decylbiphenyl-4-yl 5-*n*-hexylthiophene-2-carboxylate (A) and TBDA (B). (●) indicates mesophase-mesophase transition and (◆) recrystallization at a cooling rate of approximately $3^{\circ}\text{C min}^{-1}$.

higher homologues are reached and the member $n = 9$ does not give a crystal J phase due to the onset of crystallization.

2.3. 4'-*n*-Ocylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (1: $m = 8$; $n = 1-10$)

This homologous series exhibits similar liquid crystal properties to the corresponding nonyl and decyl homologues except that the octyl compounds do not give rise to S_F phases. All ten member possess an enantiotropic nematic mesophase and the plot (see figure 3) shows that the points for the N-I transition temperatures follow the same trend as that for the nonyl homologues. As with the nonyl homologues, the early members (in this instance $n = 3, 4$, and 5) give rise to a monotropic crystal G phase and the change to smectic polymorphism commences at $n = 6$. However, the S_1 phase of the members $n = 6, 7$, and 8 passes directly to the crystal J phase on cooling without the incursion of the S_F phase shown by the nonyl and decyl homologues. At the S_1 -CrJ transition, the schlieren texture of the S_1 phase gives rise to the mosaic texture of the crystal J phase which is quite different in appearance to the schlieren-mosaic of an S_F phase. The existence of higher order smectic phases for the members $n = 7-10$ is prevented by the occurrence of crystallization at a higher temperature than for the decyl counterparts.

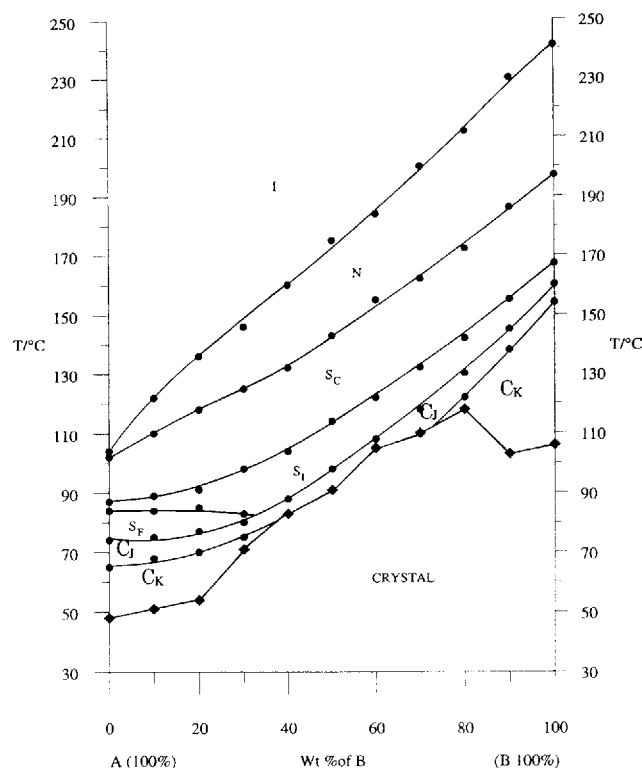


Figure 6. Binary phase diagram for mixtures (wt %) between 4'-*n*-decylbiphenyl-4-yl 5-*n*-octylthiophene-2-carboxylate (A) and HEPTOBPD (B). (●) indicates mesophase-mesophase transition and (◆) recrystallization at a cooling rate of approximately $3^{\circ}\text{C min}^{-1}$.

3. Experimental

3.1. Analysis

Structural confirmation of the structures of the intermediates and the products was obtained by ^1H NMR spectroscopy (either Hitachi Perkin-Elmer R24-b 60 MHz spectrometer or JEOL FX60Q 270 MHz spectrometer) with tetramethylsilane as internal standard and infrared spectroscopy (Perkin-Elmer 157 grating spectrophotometer). Mass spectra were determined with an A.E.I. MS 902S spectrometer equipped with a Mass Spectrometry Services 200 console and an INCOS 2300 data system. By hplc, the purity of the esters was established as 99.5 per cent or better.

Thermal analysis was carried out with a Perkin-Elmer DSC7 differential scanning calorimeter and thermal optical microscopy with a Vickers M75 polarizing microscope in conjunction with a Mettler FP52 hot stage and FP5 control unit.

3.2. Synthetic methods

The synthesis of several 5-*n*-alkylthiophene-2-carboxylic acids is reported in the literature [8-11]. In the present work the route reported by Pomonis *et al.* [11], was used. Each *n*-alkanoyl chloride, prepared by heating the

Table 4. Transition temperatures ($^{\circ}\text{C}$) and enthalpies ($\Delta H/\text{kJ mol}^{-1}$) (in italics) for the 4'-*n*-decylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates.

<i>n</i>	Cr-Cr	Cr-N	N-I	S _C -I	S _C -N	S _I -N	CrG-N	S _I -S _C	S _F -S _I	CrJ-S _f	CrK-CrJ	N-Cr
1		99.9 <i>28.00</i>	115.8 <i>0.78</i>									64.4 <i>22.80</i>
2	69.5 <i>25.66</i>	72.9 <i>1.28</i>	106.4 <i>0.81</i>				(63.0) <i>5.54</i>					CrG-Cr 18.4 <i>14.00</i>
3	73.6 <i>11.80</i>	75.7 <i>0.19</i>	104.9 <i>1.57</i>				—†					72.5 <i>10.90</i>
4		Cr-CrK 69.0 <i>12.80</i>	99.9 <i>1.08</i>				78.4 <i>8.42</i>		—	—	—	CrK-Cr 20.9 <i>8.07</i>
5		68.5	103.5		83.6			82.3	—	79.0	77.5	23.2
6		<i>14.40</i>	<i>1.02</i>				5.85‡			0.09	0.06	24.70
		62.7 <i>12.52</i>	100.0 <i>1.67</i>		89.1 <i>4.32</i>			84.2 <i>2.60</i>	—	74.6 <i>0.16</i>	—	43.4 <i>9.58</i>
7		Cr-CrJ 74.0 <i>14.97</i>	103.0 <i>1.70</i>		94.7 <i>3.51</i>			82.9 <i>2.42</i>	—	74.3 <i>0.18</i>	(—)	42.0 <i>11.03</i>
8		Cr-S _F 71.3 <i>15.61</i>	103.3 <i>1.97</i>		99.3 <i>4.58</i>			83.3 <i>2.27</i>	—	(69.6) <i>0.24</i>	(—)	43.7 <i>10.70</i>
9		77.5 <i>18.46</i>	104.5 <i>2.52</i>		102.6 <i>4.41</i>			81.8 <i>1.89</i>	—	(66.3) <i>0.12</i>	(—)	41.0 <i>12.99</i>
10		73.7 <i>16.59</i>		102.7 <i>8.12</i>				79.2 <i>1.59</i>	—	(56.2) <i>0.78</i>		CrJ-Cr 34.2 <i>9.81</i>

Symbols have their usual meaning: Cr, crystal; N, nematic; S_A, smectic A; CrJ, crystal J; I, isotropic liquid, etc. Thus, Cr-N indicates the temperature (m.p.) at which the crystal (Cr) melts to the nematic phase (N).

Temperature of crystallization (at a cooling rate of approximately $3^{\circ}\text{C min}^{-1}$).

Values in parentheses are for monotropic transitions.

† Transition detected by optical microscopy, but not differential scanning calorimetry.

‡ Enthalpy value for two unresolved peaks.

appropriate carboxylic acid with thionyl chloride, was distilled and used immediately to give the corresponding 2-acylthiophene by Friedel-Crafts acylation of thiophene in the presence of tin(IV) chloride (which caused minimal ring-opening of the thiophene nucleus) as the Lewis acid catalyst. Reduction of the 2-acylthiophene by the Huang-Minlon modification of the Wolff-Kishner reaction gave the appropriate 2-*n*-alkylthiophene which was lithiated at the 5-position with *n*-butyllithium. Treatment with solid carbon dioxide followed by appropriate work-up then gave the required 5-*n*-alkylthiophene-2-carboxylic acid.

The 4-hydroxy-4'-*n*-octyl-, -nonyl- and -decylbiphenyls were prepared from 4-cyano-4'-propyloxybiphenyl. Treatment of this cyano-compound with the appropriate Grignard reagent afforded the required 4-*n*-alkanoyl-4'-propyloxybiphenyl which, on reduction by the Huang-Minlon-Wolff-Kishner method, gave the corresponding 4-*n*-alkyl-4'-propyloxybiphenyl. Cleavage of the propyl ether linkage with hydrobromic acid [12] then afforded the required 4-*n*-alkyl-4'-hydroxybiphenyl.

3.3. Materials

3.3.1. *n*-Alkanoyl chlorides

The appropriate *n*-alkanoic acid (0.36 mol) was heated under reflux with thionyl chloride (100 g, 1.0 mol) for 2 h after which the excess of thionyl chloride was removed, the residue distilled, and the resulting pure *n*-alkanoyl chloride, a clear liquid, then used without delay.

3.3.2. 2-Acylothiophenes

Tin(IV) chloride (35 g, 0.135 mol) was added, dropwise with efficient stirring, to a solution of the appropriate *n*-alkanoyl chloride (0.27 mol) in dry dichloromethane (225 cm³) maintained at 0–5° throughout the addition. Stirring was continued for 1 h, whereafter the reaction mixture was poured into 2 M aqueous hydrochloric acid (450 cm³) and ice. After stirring vigorously for 1 h, the organic layer was separated and washed with aqueous NaHCO₃ (2 × 200 cm³), water (200 cm³), and dried (MgSO₄). The solvent was removed and the residue distilled under reduced pressure to give the 2-acylthio-

phene (75–90 per cent) as a clear liquid. B.p.s were in good agreement with those reported in the literature [13–15].

The following spectroscopic data refer to 2-*n*-decanoylthiophene: ν_{\max} (thin film) 3100 (arom. C–H str.) 2920, 2850, 1665 (C=O str.). 1415, 1355, 1233, 857 (2-subst. thiophene [10]), 718 cm^{-1} ; δ_{H} (CDCl_3) 0.89 (3 H, t, CH_3), 1.27 (14 H, m, alkyl CH_2), 2.89 (2 H, t, COCH_2) 7.04–7.75 (1 H, m; 2 H, m, 2-subst. thiophene) ppm.

3.3.3. 2-*n*-Alkylthiophenes

A mixture of the appropriate 2-acylthiophene (0.18 mol), hydrazine hydrate (45 g, 0.9 mol), and diethylene glycol (360 cm^3) was heated for 2.5 h during which the temperature of the mixture was slowly raised to 210°C and 50 cm^3 of distillate was removed. The mixture was cooled, potassium hydroxide (50.4 g, 0.9 mol) added, and the temperature raised to and maintained at 210°C for a further 3 h. After cooling, the mixture was acidified with concentrated hydrochloric acid and shaken with chloroform (3 \times 300 cm^3). The combined extracts were washed with water (300 cm^3), dried (Na_2SO_4), the solvent removed, and the residue purified either by vacuum distillation or column chromatography on silica gel, eluting with light petroleum (b.p. 40–60°C), to give the 2-*n*-alkylthiophene (40–70 per cent) as a clear oil. B.p.s corresponded with those reported in the literature [13, 15].

A more suitable procedure for lower boiling homologues, for example, 2-*n*-propylthiophene, was to heat the reaction mixture at 145°C, under reflux, for 1 h after the addition of KOH. The temperature of the reaction mixture was then raised to 210°C, as the product was allowed to distil off. The product was then extracted from the distillate with chloroform, and isolated as described above.

The following spectroscopic data for 2-*n*-decylthiophene are typical of the series: ν_{\max} (thin film) 2065 (arom. C–H str.), 2920, 2850, 1463, 1438, 1375, 850, 818 (2-subst. thiophene) cm^{-1} ; δ_{H} (CDCl_3) 0.90 (3 H, t, CH_3), 1.27 (16 H, m, alkyl CH_2), 2.80 (2 H, t, CH_2), 6.63–7.07 (3 H, m, 2-subst. thiophene) ppm.

3.3.4. 5-*n*-Alkylthiophene-2-carboxylic acids

1.6 M *n*-Butyllithium in hexane (16.25 cm^3 , 0.026 mol) was added, with stirring over 20 min at -10°C , to the appropriate 2-*n*-alkylthiophene (0.026 mol) in dry ether (70 cm^3), under nitrogen. The reaction mixture was allowed to warm to room temperature, stirred for a further 90 min, and then poured onto a large excess of powdered solid CO_2 , under nitrogen. The mixture was stirred for a further 60 min, allowed to warm to room temperature, and water (100 cm^3) added prior to the final 10 min of stirring. The aqueous and organic layers were separated and the aqueous layer was acidified with concentrated hydrochloric acid and cooled in ice. The resulting carboxylic acid,

if released as a solid, was filtered off and purified by recrystallization as described below. If the product was not obtained as a solid at this stage, the acidified solution/emulsion was shaken with ether (3 \times 50 cm^3), and the extracts were combined, dried (Na_2SO_4), and the solvent evaporated off. The solid residue was then recrystallized twice from hexane and from light petroleum (b.p. 40–60°C). The 5-*n*-alkylthiophene-2-carboxylic acids (40–70 per cent) were obtained as colourless crystalline solids, m.p.s (°C): CH_3 136–137 (lit. [8] 136); C_2H_5 70–71 (71 [8, 9]); C_3H_7 57.2–58.5 (59 [8]); C_4H_9 52–53 (52 [8]); C_5H_{11} 69–70 (70 [9]); C_6H_{13} 63–64 (63 [8]); C_7H_{15} 73–74 (73 [8]); C_8H_{17} 74–75 (75 [8, 9]); C_9H_{19} 76–77 (75–76 [11]); $\text{C}_{10}\text{H}_{21}$ 82–83 (83–84) [10].

The following spectroscopic data refer to 5-*n*-decylthiophene-2-carboxylic acid, and are typical of the series: ν_{\max} (KBr) 3000 (OH str., br), 2953, 2918, 2848, 1682 (C=O str.), 1465, 1296 (C–O str.), 938, 753, 724 cm^{-1} ; δ_{H} (CDCl_3) 0.88 (3 H, t, CH), 1.25 (16 H, s, alkyl CH), 2.85 (2 H, t, CH), 6.81 and 7.71 (2 H, dd, 2,5-disubst. thiophene), 9.69 (1 H, s, CO_2H , exchanges with D_2O) ppm.

3.3.5. 4-*n*-Alkanoyl-4'-*n*-propyloxybiphenyl

4-Cyano-4'-*n*-propyloxybiphenyl (42 g, 0.18 mol) in dry tetrahydrofuran (200 cm^3) was added, at room temperature during 30 min, to the appropriate Grignard reagent, prepared in the usual manner from the corresponding *n*-alkyl bromide (0.18 mol) and magnesium (4.8 g, 0.20 mol) in dry tetrahydrofuran (160 cm^3). The reaction mixture was heated under reflux for 1.5 h, cooled, 10 per cent aqueous hydrochloric acid (400 cm^3) added slowly with stirring, then left to stand overnight and shaken with dichloromethane (2 \times 300 cm^3). The extracts were combined, dried (Na_2SO_4), the solvent removed under reduced pressure, and the residue recrystallized from methylated spirit. The 4-*n*-alkanoyl-4'-*n*-propyloxybiphenyls (53–75 per cent) were obtained as colourless crystalline solids, m.p.s/mesophase transition temperatures (°C) (lit. [16] °C): $\text{C}_7\text{H}_{15}\text{CO Cr-S}_E$ 118.1 (118.0), $\text{S}_E\text{-S}_A$ 120.3 (121.0), $\text{S}_A\text{-I}$ 144.7 (145.2); $\text{C}_8\text{H}_{17}\text{CO Cr-S}_E$ 113.6 (115.0), $\text{S}_E\text{-S}_A$ 120.5 (120.3), $\text{S}_A\text{-I}$ 143.1 (143.0); $\text{C}_9\text{H}_{19}\text{CO Cr-S}_E$ 107.6 (106.0), $\text{S}_E\text{-S}_A$ 118.2 (119.5), $\text{S}_A\text{-I}$ 140.2 (141.0).

The following spectroscopic data for 4-*n*-octanoyl-4'-propyloxybiphenyl are typical of the series: ν_{\max} (KBr) 2952, 2922, 2865, 1681 (C=O str.), 1602, 1260, 1195, 811 cm^{-1} ; δ_{H} (CDCl_3) 0.69–2.16 (18 H, m, alkyl CH_2 , CH_3), 2.97 (2 H, t, COCH_2), 3.97 (2 H, t, ArOCH_2), 6.90–8.68 (8 H, m, ArH) ppm.

3.3.6. 4-*n*-Alkyl-4'-*n*-propyloxybiphenyls

A mixture of the appropriate 4-*n*-alkanoyl-4'-*n*-propyloxybiphenyl (0.13 mol), 99 per cent hydrazine hydrate (37.5 g, 0.75 mol), and potassium hydroxide (37.5 g,

0.67 mol) in diethylene glycol (235 cm³) was heated under reflux, with stirring, at 110°C for 10 h. Distillate was then removed from the reaction mixture until the temperature of the liquid remaining in the flask reached 180°C. Care was required as the reaction became noticeably exothermic at approximately 130°C. The temperature was maintained at 180°C for 8 h and the mixture was then cooled, poured into water (400 cm³), and shaken with dichloromethane (2 × 350 cm³). The combined extracts were washed with (2 × 350 cm³), dried (MgSO₄), the solvent removed under reduced pressure, and the residue recrystallized from methylated spirit. The 4-*n*-alkyl-4'-*n*-propyloxybiphenyls (85–95 per cent) were obtained as a pale yellow crystalline solids, m.p.s (°C): C₈H₁₇ 70–70.5, C₉H₁₉ 69–70, C₁₀H₂₁ 72–73.

The following spectroscopic data are for 4-*n*-octyl-4'-*n*-propyloxybiphenyl: ν_{\max} (KBr) 2962, 2918, 2847, 1608, 1501, 1256, 810 cm⁻¹; δ_{H} (CDCl₃) 0.61–2.10 (20 H, m, alkyl CH₂, CH₃), 2.62 (2 H, t, OCH₂), 6.92–7.95 (8 H, m, ArH) ppm.

3.3.7. 4-*n*-Alkyl-4'-hydroxybiphenyl

Acetic anhydride was added, with stirring over 5 min, to the appropriate 4-*n*-alkyl-4'-*n*-propyloxybiphenyl (0.05 mol) in a mixture of glacial acetic acid (35 cm³) and 48 per cent aqueous hydrobromic acid (35 cm³). The reaction mixture was heated under reflux for 18 h, then cooled, water (250 cm³) added, and, after the continuation of stirring for a further 30 min., shaken with dichloromethane (4 × 125 cm³). The combined extracts were washed with water (2 × 250 cm³), dried (MgSO₄), and the solvent removed under reduced pressure. The residue was purified by flash chromatography [17] on a silica gel column, eluting with chloroform, followed by recrystallization chloroform–light petroleum (b.p. 60–80°C). The 4-*n*-alkyl-4'-hydroxybiphenyls (25–35 per cent) were obtained as colourless crystalline solids, m.p.s (°C) (lit. [18] °C): C₈H₁₇ 139–139.5; C₉H₁₉ 139–140 (139–140); C₁₀H₂₁ 141–141.5 (142).

The following spectroscopic data refer to 4-hydroxy-4'-*n*-octylbiphenyl: ν_{\max} (KBr) 3430 (OH str., br.), 2955, 2920, 2850, 1678, 1598, 1499, 1267, 812 cm⁻¹; δ_{H} (CDCl₃) 0.72–1.90 (15 H, m, alkyl CH₂, CH₃) 2.62 (2 H, t, ArCH₂), 5.14 (1 H, s, OH, exchanges with D₂O), 6.78–7.62 (8 H, m, ArH) ppm.

3.3.8. 4'-*n*-Alkylbiphenyl-4-yl 5-*n*-alkylthiophene-2-carboxylates (1)

Trifluoroacetic anhydride (0.5 g, 0.0025 mol) was added to the appropriate 4-*n*-alkyl-4'-hydroxybiphenyl (0.002 mol) and 5-*n*-alkylthiophene-2-carboxylic acid (0.002 mol) in dry dichloromethane (50 cm³) and the mixture was stirred for 10–15 h protected from atmospheric moisture. When the esterification was complete

(tlc) the solvent was removed under reduced pressure and the residue was purified by column chromatography, firstly on neutral alumina (Brockmann grade 1), eluting with chloroform, and then on silica gel, eluting with toluene–light petroleum (b.p. 60–80°C). The ester was recrystallized from ethanol and from light petroleum (b.p. 60–80°C) until the m.p. and N–I transition temperatures remained constant. The yields after one crystallization were 35–60 per cent. The purity of the esters was ≥ 99.5 per cent by hplc. M.p.s and liquid crystal transition temperatures are listed in tables 1, 2, and 3.

The spectroscopic characteristics of the esters of the three homologous series investigated are very similar and the following data refer to 4'-*n*-decylbiphenyl-4-yl 5-*n*-decylthiophene-2-carboxylate: Found: C, 79.0, H, 9.72 per cent; m/z 560 (15 per cent), 251 (100). C₃₇H₅₂O₂S requires C, 79.28, H, 9.28 per cent; M , 560; ν_{\max} (KBr) 2957, 2922, 2852, 1715 (C=O str.), 1492, 1453, 1283, 1167, 797, 745 cm⁻¹; δ_{H} (CDCl₃) 0.70–1.98 (38 H, m, alkyl CH₂, CH₃), 2.49–3.04 (4 H, m, ArCH₂), 6.80–7.88 (10 H, m, ArH) ppm.

3.3.9. 4'-*n*-Alkylbiphenyl-4-yl 4-*n*-alkylbenzoates (2)

These esters were prepared in an analogous manner from the appropriate 4-*n*-alkyl-4'-hydroxybiphenyl and 4-*n*-alkylbenzoic acid. Liquid crystal transition temperatures are given in the text.

The following spectroscopic data refer to 4'-*n*-decylbiphenyl-4-yl 4-*n*-decylbenzoate: Found: C, 84.99, H, 9.88 per cent; m/z 554 (15 per cent), 245 (100). C₃₉H₅₄O₂ requires C, 84.47, H, 9.75 per cent; M 554; ν_{\max} (KBr) 2958, 2920, 2857, 1730 (C=O_{str.}) 1495, 1468, 1275, 1080, 810, 720 cm⁻¹; δ_{H} (CDCl₃) 0.9 (6 H, t, 2 × CH₃), 1.2–1.3 (28 H, m, alkyl CH₂), 1.7 (4 H, m, 2 × ArCH₂CH₂), 2.7 (4 H, m, 2 × ArCH₂), 7.2–8.2 (12 H, m, ArH) ppm.

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