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Masahiko Sahara[a]; Shinichi Yano[a]; Kenichi Ikemoto[b]; Kazuo Maejima[c]
[a] Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan [b] Sanko Kaihatsu Kagaku Kenkyusyo Co., Ltd., Shiga, Japan [c] Chemical Research Institute, Sekisui Chemical Co., Ltd., Osaka, Japan

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Mesomorphic phase transitions of 4,4‴-dialkyloxyquaterphenyls and dialkyl quaterphenyl-4,4‴-dicarboxylates

by MASAHIKO SAHARA, SHINICHI YANO*, KENICHI IKEMOTO† and KAZUO MAEJIMA‡

Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-11, Japan

† Sanko Kaihatsu Kagaku Kenkyusyo Co., Ltd., 657-1 Shimonogou, Moriyama, Shiga 524, Japan

‡ Chemical Research Institute, Sekisui Chemical Co., Ltd., 2-1 Hyakuyama, Shimamoto, Mishima, Osaka 618, Japan

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The mesogenicities of 4,4‴-dialkyloxyquaterphenyls (DAQP) and dialkyl quaterphenyl-4,4‴-dicarboxylates (DCQP) were studied by differential scanning calorimetry, optical microscopy and miscibility tests. The DAQP homologues, for which the number of carbon atoms in the alkyloxy group (*n*) is 1–9, showed a S_A phase, and the higher homologues (*n* = 9–18) showed a S_C phase. The propyl, butyl and pentyl esters of DCQP showed a S_A phase, and the octyl and dodecyl esters showed S_A and S_C phases. The isopropyl, isobutyl, 2-ethylhexyl and cyclohexyl esters showed a S_C phase and the branching of the alkyl group strikingly lowered the mesophase thermal stabilities.

1. Introduction

Polyphenyls [1–4] have long been recognized as most important rigid core systems for the design of liquid crystal forming compounds. Biphenyl derivatives have been in the limelight as most popular and excellent liquid crystalline materials. A number of terphenyl derivatives have also been found to show liquid crystalline phases, but the elongated rigid core of *p*-terphenyl commonly increases the melting point (T_m) greatly, reducing their application in electro-optic devices, although some terphenyl derivatives can be used as components for increasing the clearing point in mixed systems. Recently Gray and his co-workers [5–8] have synthesized many lateral fluoro-substituted terphenyl derivatives and so succeeded in lowering T_m. Moreover, they have found that some of them have excellent properties and are applicable for electro-optic devices.

Mesogenicities of quaterphenyl derivatives have been studied by several researchers. In 1927, Vorländer [9] reported the existence of a mesophase in 4,4‴-diaminoquaterphenyl and 4,4‴-dinitroquaterphenyl. Schubert *et al.* [10, 11], found smectic C (S_C) and nematic phases in 4,4‴-di-*n*-acylquaterphenyls and a smectic phase in 4,4‴-dialkylquaterphenyls, dialkyl quaterphenyl-4,4‴-dicarboxylates and 4,4‴-bis-(5-*n*-alkyloxycarbonylpentyl)quaterphenyls. Chan *et al.* [5] also established the mesomorphic properties of a few difluorinated 4,4‴-dialkyl- and -dialkoxy-quaterphenyls obtained as by-products from certain aryl-aryl coupling reactions.

Quaterphenyl derivatives certainly have some attractive features for the design of liquid crystal compounds applicable to electro-optic devices: (i) quaterphenyl is chemically stable and the elongated rigid core may enhance the thermal stability; (ii) a combination of the elongated rigid quaterphenyl core with various flexible terminal groups can be expected to generate new functional mesomorphic properties; (iii) lateral substitution of quaterphenyl, for example by a halogen atom such as fluorine, would be expected to lower T_m and occasionally to provide excellent electro-optical properties. It seems worthwhile to study systematically the mesogenicity of quaterphenyl derivatives in order to design new or useful liquid crystal compounds.

In the previous communication [12], we briefly noted the mesomorphic properties of 4,4‴-dialkyloxyquaterphenyls ($RO{-}C_6H_4C_6H_4C_6H_4C_6H_4{-}OR$) and dialkyl quaterphenyl-4,4‴-dicarboxylates ($ROOC{-}C_6H_4C_6H_4C_6H_4C_6H_4{-}COOR$). The variation of the mesomorphic phase transitions is systematically discussed as a function of the length of the alkyloxy or alkyl groups.

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* Author for correspondence.

2. Experimental

2.1. *Materials*

4,4‴-Dialkyloxyquaterphenyls (*DAQP*). 4-Bromo-4′-alkoxybiphenyls were prepared by the alkylation of 4-bromo-4′-hydroxybiphenyl. The DAQPs were synthesized from the 4-bromo-4′-alkyloxybiphenyls by a debromination reaction; for example, a mixture of 4-bromo-4′-hexyloxybiphenyl (6·7 g, 0·02 mol), 4 *M*-aqueous KOH (10 ml), and 5 per cent Pd–C catalyst (0·9 g) and ethylene glycol (80 ml)/water (10 ml) was stirred at 110°C for 48 h. After adding water (200 ml), the reaction mixture was neutralized with HCl and the Pd–C residue was removed from the precipitate by dissolving the organic product in hot *N*,*N*-dimethylformamide (DMF) (500 ml). It was not easy to purify the DAQP products fully, because the DAQP compounds were insoluble in most solvents at room temperature and were only slightly soluble in hot toluene and DMF. The crude products were therefore recrystallized several times from DMF for the $n = 1$–3 compounds and from toluene for the $n = 4$–18 compounds. The crystals obtained were washed with methanol and fully dried in order to remove DMF/toluene, giving colourless crystals (yields: 10–20 per cent). All the DAQP homologues were identified as the required materials and judged to be fully pure from elementary analyses, DSC, IR spectroscopy and mass spectrometry: IR (KBr): 3038, 2850–2955, 1255–1260, 1025–1030, 720–730, 810–815, 495 cm^{-1}. Elementary analyses: for example C (found 85·18, calcd. 85·31 per cent), H (found 7·97, calcd. 8·00 per cent) for the $n = 5$ compound. *M*/*e*: 562, 450, 338 for the $n = 8$ compound.

Dialkyl quaterphenyl-4,4‴-dicarboxylates (*DCQP*). The alkyl esters of 4-bromobiphenyl-4′-carboxylic acid were prepared by esterification of 4-bromobiphenyl-4′-carboxylic acid with the corresponding alkanol. The DCQPs were synthesized by a debromination reaction from the alkyl 4-bromobiphenyl-4′-carboxylates using almost the same procedure as that for the DAQPs described above. IR (KBr): 2830–2970, 1716, 1265–1275, 1100–1120, 760–770, 815–830, 695–715 cm^{-1}. For example, for the butyl ester, elementary analyses: C (found 80·63, calcd. 80·60 per cent), H (found 6·81, calcd. 6·76 per cent) and *M*/*e*: 506, 450.

2.2. *Measurements*

Phase transition temperatures and the associated entropy changes were determined either by differential scanning calorimetry (Seiko–Denshi Co., SSC-5000) at a heating/cooling rate of 5 K min^{-1} or by optical microscopy. Texture observations and some of the phase transition temperature measurements were made using an Olympus BH-2 optical polarizing microscope equipped with a Linkam TH-600 RMS hot stage, when the clearing points (T_C) were higher than 573 K, and a Nikon Optiphoto-Pol XTP-11 optical polarizing microscope equipped with a Mettler FP82 hot stage, when T_C was lower than 573 K, at a heating/cooling rate of 5 K min^{-1}.

3. Results and discussion

3.1. *Phase transition of the 4,4‴-dialkyloxyquaterphenyl homologues*

The phase transition temperatures and entropy changes for the DAQP homologues are listed in table 1. The phase

Table 1. Phase transition temperatures (K) and entropy changes (J K^{-1} mol^{-1}) in parentheses of the DAQP homologues. $H_{2n+1}C_nO–C_6H_4C_6H_4C_6H_4C_6H_4–OC_nH_{2n+1}$.

n	Cr$_1$		Cr$_2$		Cr$_3$		Cr$_4$		S$_C$		S$_A$		I
1	•	604 (17)	•		—		—	626 (21)	—		•	665†	•
2	•	548 (16)	•		—		—	637 (16)	—		•	678†	•
3	•	529 (16)	•		—		—	631 (16)	—		•	680†	•
4	•	520 (17)	•	610 (8)	•		—	616 (6)	—		•	670 (15)	•
5	•	335 (29)	•	493 (16)	•	594 (13)	•	600 (9)	—		•	653 (14)	•
6	•	344 (17)	•	476 (14)	•		—	587 (20)	—		•	640 (14)	•
7	•	380 (39)	•	454 (5)	•	463 (15)	•	580 (23)	—		•	623 (16)	•
8	•	353 (10)	•	481 (8)	•		—	575 (24)	—		•	618 (19)	•
9	•	396 (57)	•	439 (5)	•	453 (14)	•	566 (22)	•	597 (3)	•	600 (15)	•
10	•	397 (53)	•	433 (13)	•	449 (14)	•	558 (23)	•		—	589 (22)	•
11	•	409 (72)	•	427 (16)	•	447 (14)	•	549 (25)	•		—	579 (25)	•
12	•	403 (68)	•	422 (16)	•	446 (13)	•	545 (26)	•		—	573 (26)	•
13	•	412 (76)	•	418 (7)	•	445 (7)	•	539 (25)	•		—	565 (24)	•
14	•	411 (109)	•	445 (11)	•		—	534 (25)	•		—	558 (24)	•
15	•	415 (122)	•	444 (11)	•		—	529 (26)	•		—	550 (28)	•
16	•	414 (136)	•	444 (11)	•	524 (28)	•	533 (5)	•		—	546 (25)	•
17	•	416 (162)	•	444 (10)	•		—	519 (36)	•		—	542 (31)	•
18	•	404 (74)	•	464 (9)	•		—	525 (33)	•		—	542 (26)	•

Transition temperatures determined by extrapolation from miscibility tests.

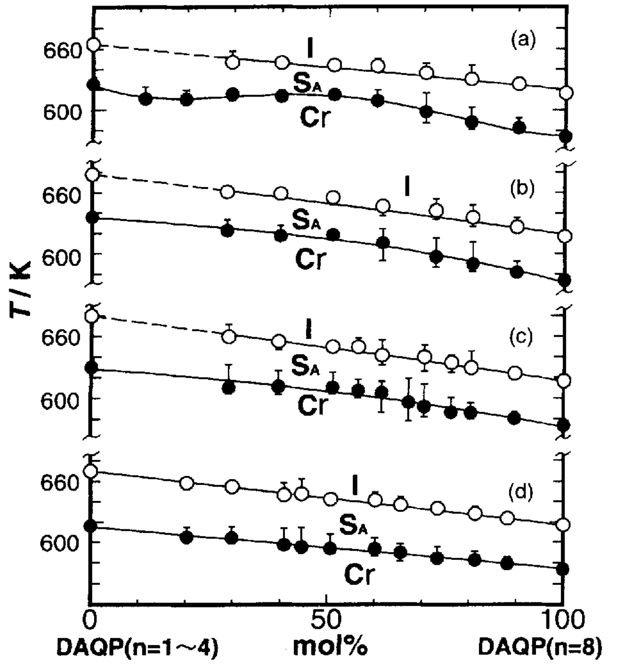

Figure 1. Phase diagrams of four binary systems with DAQP ($n = 8$): (*a*) DAQP ($n = 1$); (*b*) DAQP ($n = 2$); (*c*) DAQP ($n = 3$); (*d*) DAQP ($n = 4$). Cr, crystal; S_A, smectic A; I, isotropic liquid.

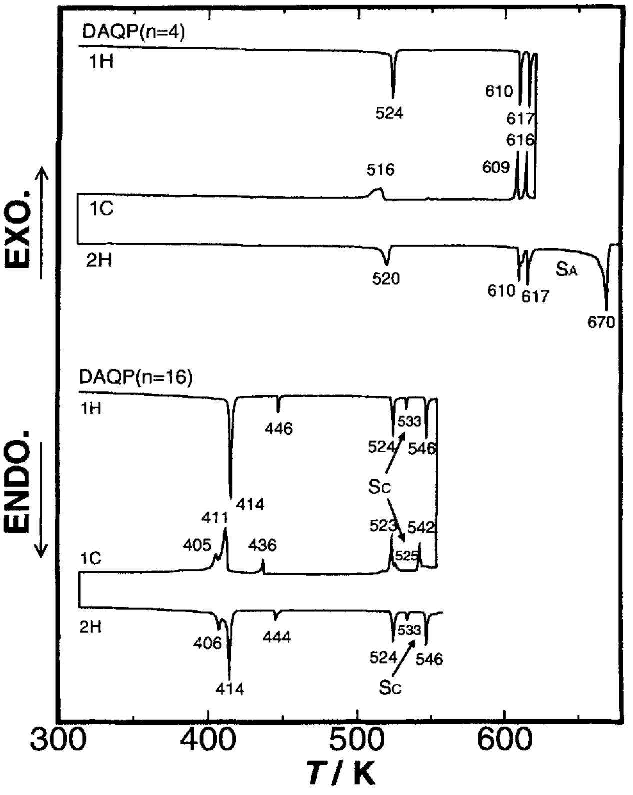

Figure 2. Schematic DSC curves for the $n = 4$ and 16 DAQP homologues at a heating/cooling rate of 5 K min^{-1}: 1H and 2H, 1st and 2nd heating processes, respectively; 1C, 1st cooling process.

transition temperatures were determined by DSC for the homologues higher than $n = 11$ and by polarizing microscopy for the $n = 5$–10 homologues. The types of mesomorphic phases were identified from texture observations using polarizing optical microscopy. For example, the $n = 8$ compound showed a smectic A (S_A) fan texture between 618 and 575 k, and in the $n = 9$ compound, a S_A fan texture seen from 600 K was transformed into a smectic C (S_C) broken fan texture near 597 K on cooling. In the S_C phase of the $n = 10$ compound, both broken fan and schlieren textures were simultaneously observed for the S_C phase.

For the $n = 1$–4 compounds, we could not identify the type of mesomorphic phase by texture observations because of rapid sublimation. Therefore, we identified the phase miscibility tests with the $n = 8$ compound. The results for the $n = 1$–4 compounds are shown in figure 1. The phase diagrams clearly show that the $n = 1$–4 compounds have a S_A phase. The plots of T_C versus the $n = 8$ content form a straight line, indicating that the mixtures behave almost as regular solutions. T_Cs were estimated by an extrapolation to 0 per cent of the $n = 8$ component. The data are shown in table 1.

DSC curves for the $n = 4$ homologue are shown in figure 2. The curves show peaks for two transitions near 610 and 616 K. Two similar peaks were also observed near 594 and 600 K for the $n = 5$ homologue (see table 1).

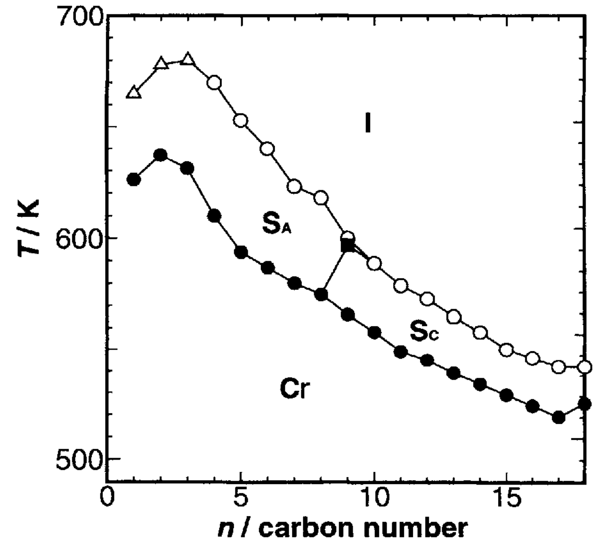

Figure 3. Phase transition temperatures (T) versus the number of carbon atoms in the alkyloxy group (n) for the DAQP homologues. Cr, crystal; S_A, smectic A; S_C, smectic C; I, isotropic liquid.

Table 2. Phase transition temperatures (K) and entropy changes ($\mathrm{J\,K^{-1}\,mol^{-1}}$) in parentheses of the DCQP homologues. $R\mathrm{OOC{-}C_6H_4C_6H_4C_6H_4C_6H_4{-}COO}R$.

Compound	*R*	$\mathrm{Cr_1}$		$\mathrm{Cr_2}$		$\mathrm{Cr_3}$		$\mathrm{S_C}$		$\mathrm{S_A}$		I
DCQP (*n* = 3)	propyl	●	423 (30)	●		—	537 (16)	—		●	657 (3)	●
		●		—		—	542†	—		—	629†	●
DCQP (*n* = 4)	butyl	●	450 (25)	●		—	516 (16)	—		●	635 (10)	●
		●		—		—	517†	—		●	624†	●
DCQP (*n* = 5)	pentyl	●	459 (41)	●		—	503 (15)	—		●	619 (11)	●
		●				—	507†	—		—	615†	●
DCQP (*n* = 8)	octyl	●	462 (42)	●		—	472 (17)	●	553 (1)	●	572 (13)	●
		●		—		—	482†	—		—	588†	●
DCQP (*n* = 12)	dodecyl	●		—		—	454 (79)	●	527 (3)	●	534 (12)	●
		●		—		—	453†	—		—	543†	●
DCQP (i3)	isopropyl	●	463 (18)	●	481 (11)	●	497 (18)	●		—	540 (0·4)	●
DCQP (i4)	isobutyl	●	461 (1)	●		—	475 (47)	●		—	553 (0·6)	●
DCQP (2EH)	2-ethylhexyl	●		—		—	345 (56)	●		—	450 (7)	●
DCQP (CH)	cyclohexyl	●		—		—	514 (47)	●		—	534‡	●

† Data by Demus *et al.* [13]; the type of smectic phase was not determined.
‡ Transition temperature observed by optical microscopy.

These two peaks were assigned respectively to a transition involving two crystal phases and to the melting point to the $\mathrm{S_A}$ phase, identified by texture observations. Although the entropy changes of melting have small values of 6 and $9\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the $n = 4$ and 5 homologues, respectively, the sums of the entropy changes of the two transitions were 14 and $21\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for the $n = 4$ and 5 homologues, respectively, values which are comparable to the entropy changes of melting for the other homologues, as seen in table 1. DSC curves for the $n = 16$ homologue are also shown in figure 2. Three endothermic peaks are observed near 524, 533 and 546 K on heating, but the 533 K peak undergoes thermal hysteresis and is seen near 525 K on cooling. Texture observations indicated a smectic C phase between 533 and 546 K on heating and 525 and 542 K on cooling; this allowed us to judge that the phase between 533 and 524 K is a crystalline phase, despite the very small entropy change of $5\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

In figure 3, phase transition temperatures are plotted against the carbon number (n) of the alkyloxy group for the DAQP homologues. The homologues lower than $n = 8$ have a $\mathrm{S_A}$ phase and the $n = 9$ compound shows both $\mathrm{S_A}$ and $\mathrm{S_C}$ phases. The higher homologues than $n = 10$ show a $\mathrm{S_C}$ phase. As n increases, T_C gradually decreases showing an odd–even effect, after increasing an n increases from 1 to 3.

3.2. *Phase transitions of the dialkyl quaterphenyl-4,4‴-dicarboxylate homologues*

Table 2 shows the phase transition temperatures and entropy changes for the DCQP homologues; these were mainly determined from DSC data on the second heating process. The type of smectic phase was identified by texture observations. Figure 4 shows phase diagrams for binary systems of the $n = 3$–5 compounds with the $n = 8$ of DAQP homologue, confirming the existence of the $\mathrm{S_A}$ phase confirmed for the $n = 3$–5 compounds. The plots of the $\mathrm{S_A}$–I transition temperature versus DAQP ($n = 8$) content are somewhat curved, suggesting the existence of intermolecular interaction between the DAQP and DCQP molecules in the $\mathrm{S_A}$ phase. As shown in table 2, Demus *et al.* [13], reported the existence of a smectic phase for several n-alkyl esters of DCQP, but did not identify the

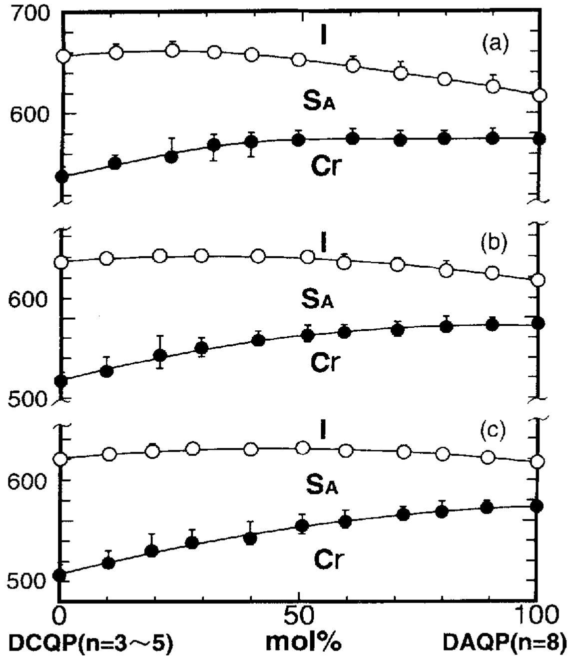

Figure 4. Phase diagrams of three binary systems with DAQP ($n = 8$): (*a*) DCQP ($n = 3$); (*b*) DCQP ($n = 4$); (*c*) DCQP ($n = 5$). Cr, crystal; $\mathrm{S_A}$, smectic A; I, isotropic liquid.

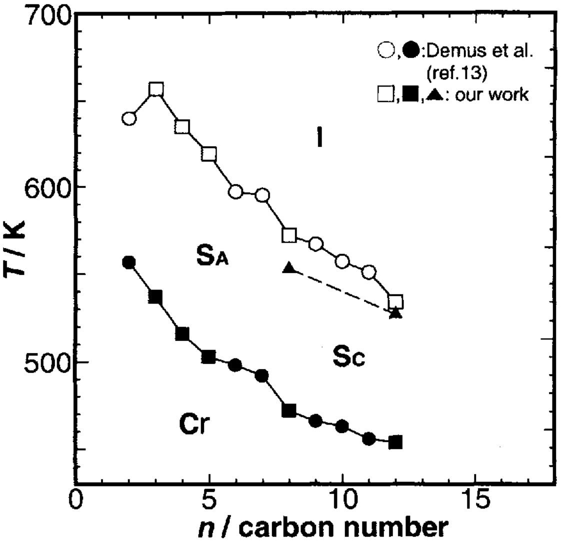

Figure 5. Phase transition temperatures (T) versus the number of carbon atoms in the n-alkyl group (n) for DCQP homologues. Cr, crystal, S_A, smectic A; S_C, smectic C; I, isotropic liquid. The type of smectic phase was not identified in the data of Demus *et al.*

type of smectic phase. However, their phase transition temperatures seem to be essentially consistent with the present data.

Figure 5 shows the phase transition temperatures as a function of the carbon number of the alkyl group (n) for the DCQP homologues: Demus's data are plotted for the $n = 2, 6, 7$ and 9–11 homologues. From our data, the $n = 3$, 4 and 5 homologues show a S_A phase, while the $n = 8$ and 12 homologues have both S_C and S_A phases. The clearing points of the smectic phase reported by Demus *et al.*, appear to be consistent with our data for the clearing points (S_A–I phase transition temperature). Therefore we can conclude that the $n = 2$ homologue would have a S_A phase, and the $n = 9$, 10 and 11 homologues would show both S_C and S_A phases, The $n = 6$ and 7 homologues should have a S_A phase, but we cannot be sure whether or not a S_C phase exists.

Phase transition parameters for branched alkyl esters of DCQP, the isopropyl, isobutyl and 2-ethylhexyl esters, are also listed in table 2. The branching of the alkyl group of course decreases the thermal stability of the smectic mesophase, compared with that of the n-alkyl esters. It is noted that the branched alkyl esters prefer to have a S_C phase. This result is known for other fluid crystal systems, and provides us with information relevant to designing quaterphenyl derivatives having a S_C^* phase.

3.3. *Mesogenicity of quaterphenyl derivatives*

Homologous series of poly-p-phenyls have been studied by several researchers [1–4]; p-quaterphenyl crystals melt into the isotropic phase near 593 K, showing no mesophase, but p-quinquephenyl shows a nematic phase between 663 and 698 K, and p-sexiphenyl shows a S_A phase between 713 and 748 K and a nematic phase between 748 and 838 K. The existence of the S_A phase in p-sexiphenyl having no flexible terminal group suggests that poly-p-phenyls have rather a good ability to form a lamellar phase. 4,4″-Dimethoxyterphenyl [13] is reported to have Cr 532 K a smectic 540 K N 541 K I phase transitions, while the $n = 1$ compound of DAQP shows a T_C of 665 K (see table 1). The thermal stability of DAQP ($n = 1$) is higher by about 120 K than that of 4,4″-dimethoxyterphenyl. The dipentyl ($n = 5$) and the dioctyl ($n = 8$) terphenyl-4,4″-dicarboxylates [14, 15] are reported to undergo Cr 412 K S_A 473 K I and Cr 411 K S_C 424 K S_A 543 K I phase transitions, respectively. The T_Cs for the $n = 5$ and 8 homologues of DCQP are higher by about 160 K for the $n = 5$ and 30 K for the $n = 8$ than those for the corresponding p-terphenyl homologues. The elongation of the central rigid core by one benzene ring strikingly enhances the thermal stability, but its magnitude appears to be weakened by the longer terminal groups.

In conclusion, this work establishes that DAQP and DCQP homologues have smectic A and/or C phases with good thermal stability, which derives from the quaterphenyl moiety.

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