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Liquid crystalline model compounds based on 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA)

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3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was investigated as the central core unit in mesogenic molecules. Of particular interest was whether the BPDA unit could be self-constrained into a *trans*-conformation, and thus organize into a liquid crystalline phase. Two homologous series of symmetrical substituted model compounds, 3,3′,4,4′-biphenyltetracarboxy-*N*,*N*′-bis-(4-*n*-alkylphenyl)diimides and 3,3′,4,4′-biphenyltetracarboxy-*N*-*N*′-bis-(4-*n*-alkoxyphenyl)diimides were synthesized. For both series high temperature smectic A phases were observed. To our knowledge these are the first examples of liquid crystalline behaviour observed with BPDA as the mesogenic core.

1. Introduction

3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) is a common dianhydride which is often used instead of pyromellitic dianhydride (PMDA) in high performance aromatic polyimides [1,2]. Upilex S®, a commercial polyimide made of BPDA and *p*-phenylene diamine, has several advantages compared to Kapton® [3], for example excellent stability in aqueous bases, lower moisture regain, higher tensile strength and modulus. It has a comparable dielectric constant but its coefficient of thermal expansion is almost a magnitude lower than that of Kapton® [4]. Some of these benefits are contributed to the BDPA moiety. As illustrated in figure 1 BPDA can rotate around the 1,1′-biphenyl bond and form a *trans*- or a *cis*-conformation. This capability has obvious consequences on the shape of the molecule, but more importantly it affects the polymer chain stiffness, when the BDPA units are connected by rigid segments [5]. The *cis*-conformation results in a chain with a certain degree of flexibility, that can be transformed and oriented into an extended rigid chain by external forces such as fibre spinning or drawing processes. After such an orientation, the polymer chains almost exclusively exist in the trans conformation. Kaneda *et al.* [6,7], and Cheng *et al.* [8–10], utilized this feature to prepare highly aligned aromatic polyimide fibres with excellent mechanical properties.

In this paper we present the use of BPDA as a central core unit in mesogenic molecules. Of particular interest is whether the BPDA unit could be constrained into the *trans*-conformation, and thus organize into liquid crystalline phases. In order to answer this question we synthesized two homologous series of symmetrical model compounds. BPDA was reacted with 4-*n*-alkylanilines resulting in the 3,3′,4,4′-biphenyltetracarboxy-*N*-*N*′-bis-(4-*n*-alkylphenyl)diimide series **3a–3e** and with 4-*n*-alkoxyanilines yielding the 3,3′,4,4′-biphenyltetracarboxy-*N*-*N*′-bis-(4-*n*-alkoxyphenyl)diimide series **5a–5e**. As will be demonstrated later, we observed a smectic A ($\mathrm{S_A}$) mesophase for both series. The liquid

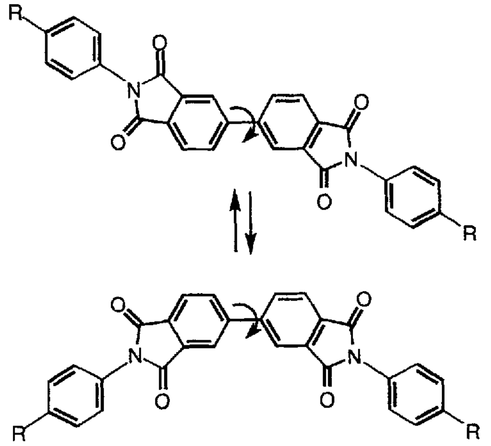

Figure 1. Schematic representation of the *cis*- and *trans*-conformation of molecules containing the 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) as the central core unit.

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crystalline behaviour was confirmed by DSC, optical microscopy and X-ray diffraction. To our knowledge these are the first examples of liquid crystalline behaviour observed for mesogenic molecules with BPDA as the central core.

2. Experimental

2.1. *Materials*

3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**1**) (BPDA) was purchased from Chriskev Company and purified twice by sublimation. 4-*n*-Butoxyaniline (**4a**), 4-*n*-hexylaniline (**2c**), 4-*n*-heptylaniline (**2d**), 4-*n*-octylaniline (**2e**) (all TCI), 4-*n*-pentyloxyaniline (**4b**) 4-*n*-hexyloxyaniline (**4c**), 4-*n*-butylaniline (**2a**), 4-*n*-pentylaniline (**2b**) (Aldrich), 4-*n*-heptyloxyaniline (**4d**) (Lancaster) and 4-*n*-octyloxyaniline (**4e**) (Kodak) were purified by vacuum distillation and used immediately.

2.2. *Characterization*

DSC measurements were carried out on a Perkin–Elmer DSC 7. The experiments were performed in the temperature range 50°–350°C with a heating and cooling rate of $10\,\mathrm{K\,min^{-1}}$. The results of the 2nd heating curve are reported. FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1600. NMR measurements were carried out on a Bruker AMX-500 MHz spectrometer at 20°C in $CDCl_3$. X-ray diffraction studies were done using a Philips flat film X-ray diffractometer (Model PW 1729). The liquid crystalline phases were assigned using a Nikon Microphot FX equipped with a Mettler hotstage FP 82. Elemental analysis was performed by Spang, Microanalytical Laboratory, 49951 Michigan.

2.3. *Synthesis*

All compounds were synthesized by a melt condensation following a general procedure. As an example for the alkylphenyl series the synthesis of 3,3′,4,4′-biphenyltetracarboxy-*N*-*N*′-bis-(4-*n*-hexylphenyl)diimide (**3c**) and for the alkoxyphenyl series the synthesis of 3,3′,4,4′-biphenyltetracarboxy-*N*-*N*′-bis-(4-*n*-hexyloxyphenyl)diimide (**5c**) are described in the following.

2.3.1. *3,3′,4,4′-Biphenyltetracarboxy-*N-N′*-bis-(4-*n*-hexylphenyl)diimide* (**3c**)

4 mmol (1·00 g) BPDA and 8·5 mmol (1·51 g) 4-*n*-hexylaniline were placed in a schlenktube under dry argon. The mixture was slowly heated up to 280°C and a homogeneous melt was obtained. During this process condensation of water was observed. After 6 h, the resulting reaction mixture was cooled and dissolved in 70 ml boiling chloroform. The hot solution was filtered and precipitated with 30 ml of acetone. This procedure was repeated three times. The purity was checked by TLC in CH_2Cl_2:CH_3OH (100:1). Yield: 1·84 g (88 per cent). Elemental analysis ($C_{40}H_{40}N_2O_4$): Calculated: C 78·40, H 6·58, N 4·57; found: C 78·15, H 6·23, N 4·21 per cent. ^1H NMR ($CDCl_3$): δ (ppm) = 0·89 (t, 6 H, $-CH_3$), 1·31 (m, 12 H, $-(CH_2)_3$), 1·65 (m, 4 H, β-CH_2), 2·7 (t, 4 H, α-CH_2), 7·35 (s, 8 H, arom.), 8·1 (s, 4 H, arom.), 8·25 (s, 2 H, arom.). IR (KBr): $2926\,\mathrm{cm^{-1}}$ (s) aliph. C–H stretch, $2853\,\mathrm{cm^{-1}}$ (m), aliph. C–H stretch, $1772\,\mathrm{cm^{-1}}$ (s)C=O stretch Imide I, $1709\,\mathrm{cm^{-1}}$ (s) C=O stretch Imide II, $1516\,\mathrm{cm^{-1}}$ (m), C–C arom., $1383\,\mathrm{cm^{-1}}$ (s) CH_3.

2.3.2. *3,3′,4,4′-Biphenyltetracarboxy-*N-N′*-bis-(4-*n*-hexyloxyphenyl)diimide* (**5c**)

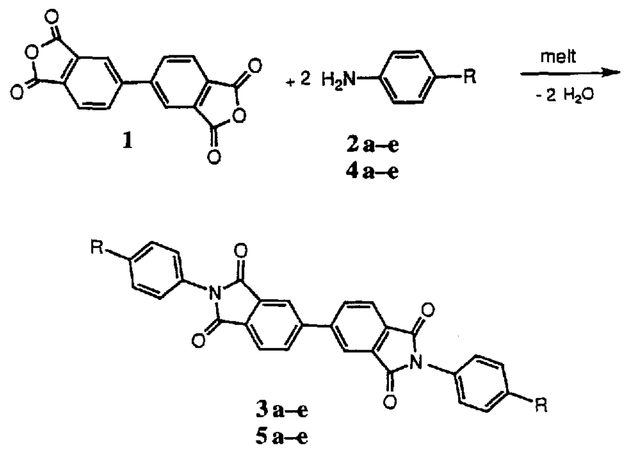
3·4 mmol (1·00 g) BPDA and 8·5 mmol (1·64 g) 4-*n*-hexyloxyaniline were transferred to a schlenktube and purged with argon. The compounds were heated slowly to 290°C and kept there for 10 h. The homogenous melt was cooled and dissolved in 60 ml of boiling chloroform. The hot and filtered solution was precipitated with 30 ml of acetone. This treatment was repeated until purity TLC was satisfactory. Yield: 1·67 g (76 per cent). Elemental analysis ($C_{40}H_{40}N_2O_6$): Calculated: C 74·51, H 6·25, N 4·34; found: C 74·68, H 6·13, N 4·39 per cent. ^1H NMR ($CDCl_3$): δ (ppm) = 0·89 (t, 6 H, $-CH_3$), 1·31 (m, 12 H, $-(CH_2)_3$), 1·65 (m, 4 H, β-CH_2), 4·0 (t, 4 H, α-CH_2), 7·35 (s, 8 H, arom.), 8·1 (s, 4 H, arom.), 8·25 (s, 2 H, arom.). IR (KBr): $2932\,\mathrm{cm^{-1}}$ (s) C–H stretch, $2870\,\mathrm{cm^{-1}}$ (m) C–H stretch, $1776\,\mathrm{cm^{-1}}$ (s) C=O stretch Imide I, $1710\,\mathrm{cm^{-1}}$ (s) C=O stretch Imide II, $1514\,\mathrm{cm^{-1}}$ (m) C–C arom., $1385\,\mathrm{cm^{-1}}$ (s) CH_3 $1252\,\mathrm{cm^{-1}}$ (m) Ar–O–C stretch.

The analytical results of all other compounds were similar. The chemical shifts are identical to the compounds reported above. The integration of the multiplet changes due to the different number of methylene units. As expected, no changes in the FT-IR spectra were observed.

3. Results and discussion

Two symmetrically substituted homologous series of *n*-alkylphenyl (**3a**–**3e**) and *n*-alkoxyphenyl (**5a**–**5e**) diimides based on BPDA as the central core were prepared. Figure 2 summarizes the synthetic route and the chemical structure of the investigated compounds. Within each homologous series the number of methylene units was varied from $n = 3$ to 7. All compounds were easily synthesized from BPDA (**1**) and the corresponding purified amines **2a**–**2e** and **4a**–**4e** by melt condensation under an inert atmosphere. The water formed during the reaction was removed by a dry argon stream. Purification from a chloroform/acetone mixture yielded the analytical pure products.

The transition data of the 2nd heating run for the *n*-alkylphenyl series **3a**–**3e** are summarized in table 1. Figure 3 shows representative DSC heating curves of compound **3a** and **3d**. Compound **3a** has two endothermic



Compound	–$(CH_2)_n$–CH_3	Compound	–O–$(CH_2)_n$–CH_3
2a,3a	$n = 3$	**4a,5a**	$n = 3$
2b,3b	$n = 4$	**4b,5b**	$n = 4$
2c,3c	$n = 5$	**4c,5c**	$n = 5$
2a,3d	$n = 6$	**4d,5d**	$n = 6$
2e,3e	$n = 7$	**4e,5e**	$n = 7$

Figure 2. Synthesis and chemical structures of a homologous series of 3,3′,4,4′-biphenyltetracarboxy-*N*,*N*′-bis-(4-*n*-alkylphenyl)diimides (**3a**–**3e**) and 3,3′,4,4′-biphenyltetracarboxy-*N*,*N*′-bis-(4-*n*-alkoxyphenyl)diimides (**5a**–**5e**).

transitions at 264·7°C and 283·1°C, which correspond to enthalpies of 33·5 kJ mol^{-1} and 8·4 kJ mol^{-1}, respectively. The latter corresponds to a clearing transition from a smectic A phase..The value of the transition enthalpy falls in the typical range observed for smectic A to isotropic transitions [11]. The smectic A phase was confirmed by polarization light microscopy. Figure 4 (*a*) displays the smectic A phase at 280°C. This picture was obtained by cooling the sample from the isotropic melt into the S_A phase. A characteristic focal-conic fan-shaped texture is shown. Discontinuity lines are clearly visible in the form of ellipse–hyperbola pairs, and homeotropic regions are observed, both typical of a S_A phase [12, 13]. Cooling the sample to 256°C, which is below the transition at 264·7°C, results in an instantaneous crystallization (see figure 4 (*b*)), where no indication of mobility was observed.

Table 1. Transition temperatures of a homologous series of 3,3′,4,4′-biphenyltetracarboxy-*N*,*N*′-bis-(4-*n*-alkylphenyl)diimides **3a**–**3e**. Enthalpies of transition are given in parentheses (in kJ mol^{-1}).

Compound	T_1†/°C	T_2†/°C	*T*/C–S_A/°C	*T*/S_A–I/°C
3a	—	—	264·7 (33·5)	283·1 (8·4)
3b	90·8 (5·7)	119·7 (5·5)	248·2 (25·9)	292·8 (10·6)
3c	—	159·2 (19·9)	240·6 (26·2)	290·1 (9·5)
3d	—	137·8 (18·8)	231·7 (24·7)	287·6 (11·1)
3e	—	155·3 (36·1)	226·0 (21·3)	280·3 (8·5)

† Solid state transitions.

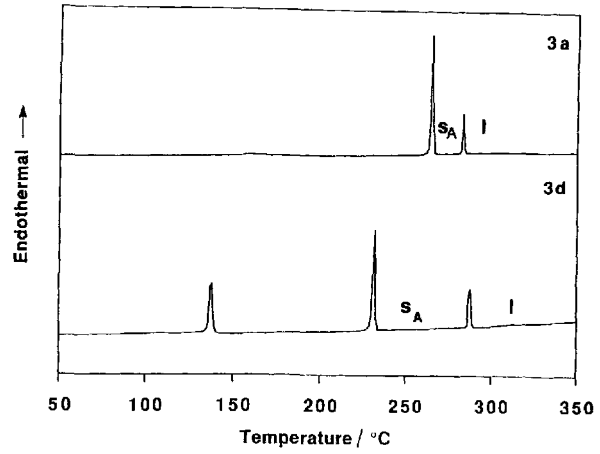
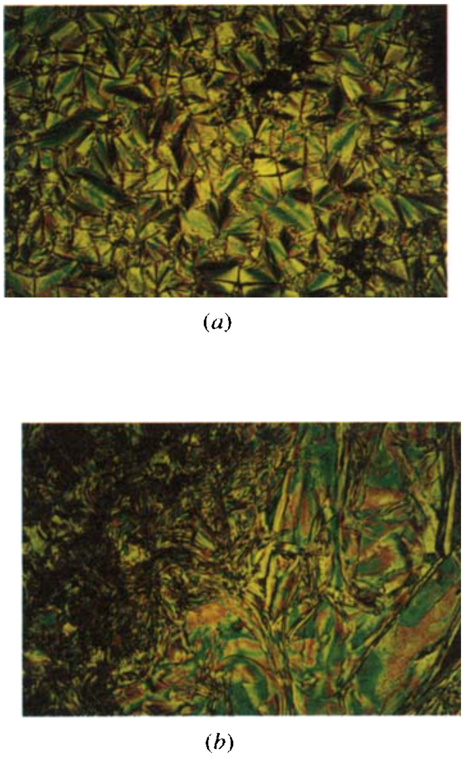


Figure 3. DSC heating curves (2nd) of compounds **3a** and **3d**.

The lower curve in figure 3 shows the heating run of sample **3d**. In this case three endothermic transitions are present. A smectic A phase was observed similar to that for **3a**. Sample **3d** melts at 231·7°C with a transition enthalpy of 24·7 kJ mol^{-1} and becomes isotropic at 287·6°C with an enthalpy of 11·1 kJ mol^{-1}. If the sample is cooled below the S_A phase the homeotropic areas become birefringent and appear similar to the textures in figure 4. The appearance of birefringence out of the homeotropic oriented regions upon cooling from a smectic A phase, implies that this phase is neither a highly ordered S_B nor S_E phase. We also see no evidence for the existence of a tilted smectic mesophase below the S_A phase, due to the fact that the enthalpies for a S_C/S_A transition are substantially lower. Since the sample also shows no macroscopic mobility, the phase is probably crystalline and consequently, the peak at 137·8°C reflects a solid state transition. Similar solid state transitions were observed for samples **3b**, **3c** and **3e**.

Plotting the transition temperatures of the homologous series **3a**–**3e** versus the number of methylene units (*n*) in the alkyl chain results in the diagram shown in figure 5. All alkylphenyl substituted compounds form smectic A mesophases. With increasing length of the terminal alkylphenyl groups the melting temperatures decrease. In agreement with the literature for a homologous series


(*a*)

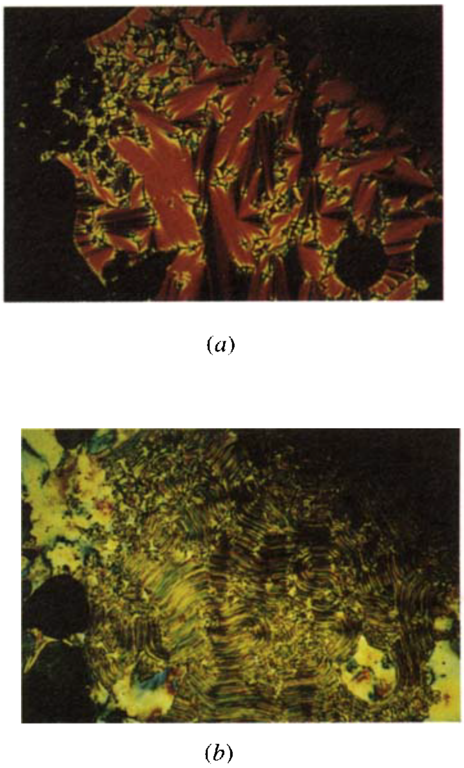
(*b*)

Figure 4. Photomicrographs between crossed polarizers of compound **3a**. (*a*) smectic A phase at 280°C (magnification × 400); (*b*) texture of solid state at 256°C (magnification × 400).

[11], the clearing points show no alternation with increasing number of methylene units. They increase until a maximum is reached at a moderate chain length, $n = 4$. A further increase of the chain length results in decreasing clearing points. The width of the S_A phase broadens with increasing length of the terminal alkyl chains from **3a–3d** and reaches a maximum for compound **3d**. The biggest change of phase stability is the variation from *n*-butylphenyl to *n*-pentylphenyl terminal groups. Some of the compounds show reproducible solid state transitions, which in some cases could be observed by a change of birefringence during polarization light microscopy studies. These transitions were not investigated further.

Wide angle X-ray investigations of the model compound **3e** were undertaken at 260°C and the sample showed the characteristic pattern of a S_A phase. The X-ray pattern exhibits a diffuse halo which corresponds to the intermolecular distance in the smectic A phase and is found at 4·8 Å. The sharp inner ring defines the layer thickness. The measured *d*-spacing is 35·9 Å. A molecular model of the compound in the most extended form showed a maximum length of the molecule to be 42·7 Å. This length would correspond to an all-*trans*-conformation of the molecule. The difference in these two values is due to coiling tendencies of the alkylphenyl terminal groups or slight interpenetration of the alkylphenyl chains. Similar X-ray studies were performed at 280°C for compound **3b** and the results confirm the assertions above. The theoretical length in the all-*trans*-conformation of the molecule **3b** should be 33·5 Å. The *d*-spacing found was 31·4 Å.


Figure 7. Photomicrographs between crossed polarizers of compound **5d**: smectic A phase at 248°C (magnification × 400).


(*a*)

(*b*)

Figure 8. Photomicrographs between crossed polarizers of compound **5c**. (*a*) smectic A phase of **5c** at 267°C (magnification × 200); (*b*) solid state texture of **5c** at 236°C (magnification × 200).

The series of *n*-alkoxyphenyl substituted diimides **5a–5e** were also examined by DSC measurements. The

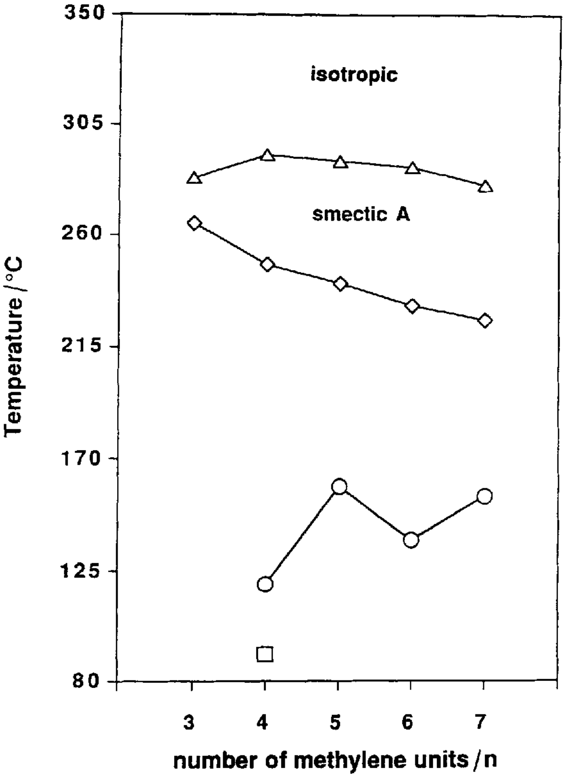


Figure 5. Transition temperatures versus the number of methylene units in the alkyl chains for the homologous series **3 a**–**3 e**. (△), Smectic A–isotropic; (◇), solid state–smectic A; (○, □), solid state transitions.

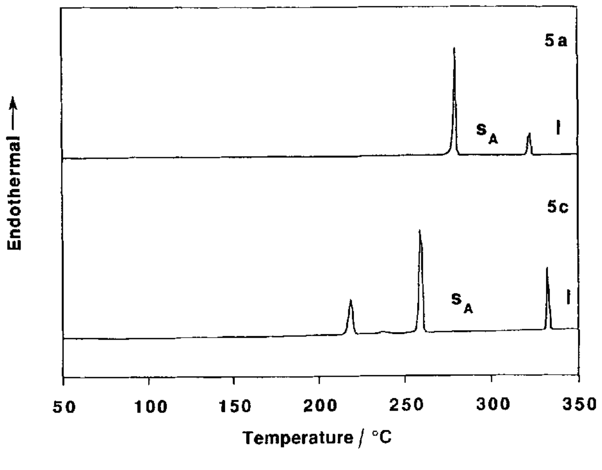


Figure 6. DSC heating curves (2nd) of compounds **5 a** and **5 c**.

results of the 2nd heating run are listed in table 2 and figure 6 illustrates the DSC heating curves of compounds **5 a** and **5 c**. Figures 7 and 8 show photomicrographs of compounds **5 c** and **5 d**. Figure 7 shows a characteristic focal-conic texture of the diimide **5 d** at 248°C. The ellipses and hyperbolas are clearly visible. Figure 8 (*a*) shows sample **5 c** at 267°C in the S_A phase. The texture shows focal-conic fans with homeotropic areas. When the sample is cooled to 236°C spontaneous crystallization occurs. As observed in the case of the alkylphenyl substituted compounds, the homeotropic areas vanish and the sample lacks macroscopic mobility. We concluded in a similar way to the alkylphenyl substituted series **3 a**–**3 e**, that there is no evidence for an additional mesophase.

The phase transitions of the homologous series **5 a**–**5 e** are plotted in figure 9. The melting and clearing points of the alkoxyphenyl series are higher compared to the alkylphenyl substituted compounds. This is commonly observed in other liquid crystalline compounds, where alkoxy groups nearly always give rise to higher liquid crystal thermal stability and melting temperatures compared to the alkyl analogues. This is a consequence of increased conjugation and rigidity of the system [14]. Also, the formation of donor/acceptor type interactions in the solid state may occur in this series. This is indicated by the yellow colour of the solid state of the alkoxyphenyl compounds, whereas the alkylphenyl compounds are white. The influence of the number of methylene units in the alkoxyphenyl series does not show a significant effect on the transition temperatures. The overall decrease in clearing points is only 15°C from **5 a** to **5 e**. The dependence on the melting points is even less distinguished. The smectic A phase has the greatest thermal stability in compound **5 c**.

To support further the fact, that all samples exhibit a smectic A mesophase, miscibility studies were carried out. Binary mixtures of compound **5 b** and **5 e**, both from the alkoxyphenyl series, were prepared. In addition, binary mixtures of **5 a** from the alkoxyphenyl series and **3 e** from the alkylphenyl series were investigated by DSC. Both resulting phase diagrams show continuous miscibility in the isotropic liquid and in smectic A phases. Co-crystal-

Table 2. Transition temperatures of a homlogous series of 3,3′,4,4′-biphenyltetracarboxy-*N*,*N*′-bis-(4-*n*-alkoxylphenyl)diimides **5 a**–**5 e**. Enthalpies of transition are given in parentheses (in kJ mol^{-1}).

Compound	T_1†/°C	T_2†/°C	T/C–S_A/°C	T/S_A–I/°C
5 a	—	—	271·9 (36·8)	314·1 (8·2)
5 b	—	—	250·2 (25·5)	312·9 (9·9)
5 c	205·9 (12·7)	223·5 (1·3)	243·8 (28·2)	312·3 (12·2)
5 d	102·7 (21·1)	225·1 (7·5)	245·4 (25·1)	306·3 (9·9)
5 e	68·7 (6·8)‡	203·9 (8·5)	244·1 (25·0)	301·2 (10·8)

† Solid state transitions.
‡ Additional peak at 63·5°C (12·9 kJ mol^{-1}).

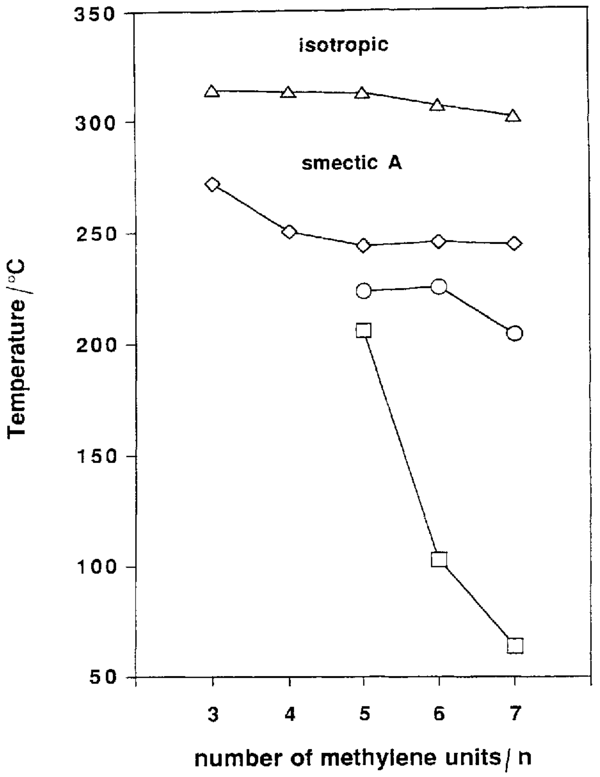


Figure 9. Phase behaviour of the homologous series **5a**–**5e** as a function of the number of methylene units in alkoxy chains. (△), Smectic A–isotropic; (◇), solid state–smectic A; (○, □), solid state transitions.

lization seems to occur in the solid state. The disappearance of some solid state transitions in the mixtures was observed.

In summary the results demonstrate that the BPDA unit is capable of being self-constrained into a *trans*-conformation, and organizing into liquid crystalline phases.

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