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Odd–even effect in biphenyl-based symmetrical dimers with methylene spacer – evidence of the B4 phase

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A series of 4-decyloxy-4′-hydroxybiphenyl esters of α,ω-alkanedicarboxylic acids containing two mesogenic units connected by a methylene spacer was synthesized. The mesogenic properties of the compounds were investigated by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction methods. A strong influence of the spacer length and its parity on the mesomorphic properties was found. A dramatic odd–even effect was observed for the clearing temperatures and entropies. Compounds with an even number of carbon atoms in the methylene spacer formed tilted smectic phases, whereas compounds with an odd number of carbon atoms in the spacer exhibited the B4 phase, characteristic of bent-shaped molecules.

Keywords: symmetric dimer; smectic phase; bent-shaped molecule; B4 phase

1. Introduction

Liquid crystalline (LC) dimers, also called twins or bimesogens, are constituted by two mesogenic moieties connected through a flexible spacer. The LC properties of such dimers are considerably influenced by the mesogenic parts as well as the type and length of the spacer.

The majority of dimeric compounds exhibit a significant odd–even effect in their mesomorphic behaviour with spacer or/and terminal tail length (*1, 2*). In particular, compounds containing a $-(CH_2)_n-$ chain as a spacer display an odd–even effect in their phase transition temperatures and entropy changes. Compounds with an odd number (n) of methylene groups exhibit lower transition temperatures than those with even n. The entropy changes at clearing transition follow clearing temperature dependence: for compounds with even n transition entropy is three times on average larger than for those with the odd n, suggesting that the orientational order is significantly different in both cases. It is assumed that odd–even effect arises from the intrinsically different molecular shapes and thus efficiency in molecular packing. If the methylene chain is in the all-trans conformation, dimers with even n have their mesogenic units nearly parallel and are rod-shaped, whereas odd homologues have mesogenic units inclined and are bent-shaped. The difference in shape results also in different size and direction of the electric dipole moment of the molecule, which could additionally affect molecular packing. In more sophisticated models the ability of the methylene chain to exist in large number of different conformations is considered, with the all-trans conformer accounting for only a small fraction of molecules. However, even taking into account the average distribution of conformations, the structure for the odd-atom spacer dimer is bent, whereas that for the even-atom is essentially linear (*3, 4*).

Usually the parity of atoms in the spacer influences clearing transitions, but in some cases also the phase type could be affected. For the series of bismesogenic compounds with 4,4′-bibenzoate units connected by methylene spacer, synthesized by Watanabe *et al.* (*5*), the even homologues formed the smectic A (SmA) phase, whereas the odd homologues formed the bilayer smectic C (SmC_2) phase.

In 1996, the polar liquid crystal structures were found for achiral compounds (*6*). The unique properties of these materials are a consequence of the close packing of bent-shaped (also called *banana-shaped* or simply *banana*) molecules. Moreover, the combination of polar order and tilt results in structural chirality of smectic layers, although the individual molecules are achiral (*7*). The bent-shaped molecules form a variety of new smectic and columnar modifications without counterpart in the field of calamitic liquid crystals. Mesostructures of such compounds represent a distinct class of thermotropic liquid crystals denoted in the literature as B-type mesophases; such nomenclature was suggested at the workshop "Banana-Shaped Liquid Crystals:

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Chirality by Achiral Molecules" held in Berlin in December 1997. Recently, a few articles reviewing the structure and nomenclature of banana phases have been published (*8, 9*).

The B-type phases are formed if the bending angle between molecular branches is 120–130 deg. Most banana-shaped liquid crystals reported so far consist of a central aromatic core, usually a phenyl ring substituted at 1,3 positions (*10, 11*). One of the most intriguing phases with large optical activity and zero birefringence is the B4 phase. Hitherto, the B4 phase was observed only for bent-shaped molecules with a central aromatic core (*12–14*). There are few models describing the structure of this phase; recently it was considered that formation of the phase is due to the instability of the flat smectic layers resulting in formation of helicoidal filaments (*15*).

However, dimers with an odd number (*n*) of methylene units in their spacer also form banana-shaped molecules. The recent discovery of a ferroelectric switching behaviour in such compounds is particularly interesting (*16*) since in the early days it was believed that a central rigid aromatic part in the molecules was essential to obtain such mesophase types. The B-phases have so far been reported for dimeric compounds having benzylideneaniline (*16*), salicylideneaniline (*17*) or benzoyloxysalicyl (*16*) mesogenic cores connected with a methylene spacer via ester (*17, 18*) or imine (*18*) linkages.

In this paper, we report the properties of dimers in which simple biphenyl moieties with decyloxy terminal chains are connected by a poly(methylene) spacer ended by carbonyloxy groups (scheme 1).

For the materials studied, depending on the parity of the carbon atoms in the spacer, either smectic phases (typical for the rod-like molecules) or the B4 phase (characteristic of bent-shaped molecules) has been observed.

2. Experimental

Instrumentation

All product structures were confirmed by FT-IR, ^{1}H NMR or ^{13}C NMR spectroscopy. The infrared spectra (in CH_2Cl_2) were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrams 2000 software, and the NMR spectra (in $CDCl_3$) were recorded using a Varian Gemini 200 MHz spectrometer. The structures were confirmed also by elemental analysis (within $\pm 0.4\%$ of theoretical values). The purity of all compounds obtained was checked by means of thin-layer chromatography using SiO_2 plates with UV indicator and chloroform as an eluent.

The phase transitions were observed using a polarising optical microscope (POM, Nikon Optiphot 2-Pol) equipped with Mettler hot stage (FE82/80HT). Differential scanning calorimetry (DSC) measurements were carried out at a scan rate of $2°C\,min^{-1}$ using a Perkin Elmer 7 calorimeter. The X-ray measurements of powder samples were carried out using X'Pert PRO Philips diffractometer with Cu K_α radiation in the low-angle range the scans were taken with Bruker Nanostar system equipped with 2D-area detector. The molecular lengths and shape were calculated with Hyperchem 6 package.

To check electric switching and for dielectric measurements, ITO cells about 3 and 5 µm thick were used.

Synthesis

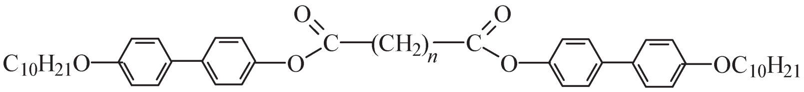
All the chemicals used were analytical grade commercial products (Aldrich) and were applied without further purification, except for 4-decyloxy-4′-hydroxybiphenol, which was synthesized using a previously reported method (*19*). The members of the series with spacer containing methylene groups (*n*) from 3 up to 12 were prepared using the same method. The 4-decyloxy-4′-hydroxybiphenyl esters of α,ω-dicarboxylic acids were prepared from the appropriate acids and 4-decyloxy-4′-hydroxybiphenol in the presence of *N,N′*-dicyclohexylcarbodiimide and a catalytic amount of *N,N*-dimethyl-4-aminopyridine (Scheme 2).

The average yield of the esters after purification (column chromatography, SiO_2, chloroform) was about 50%.

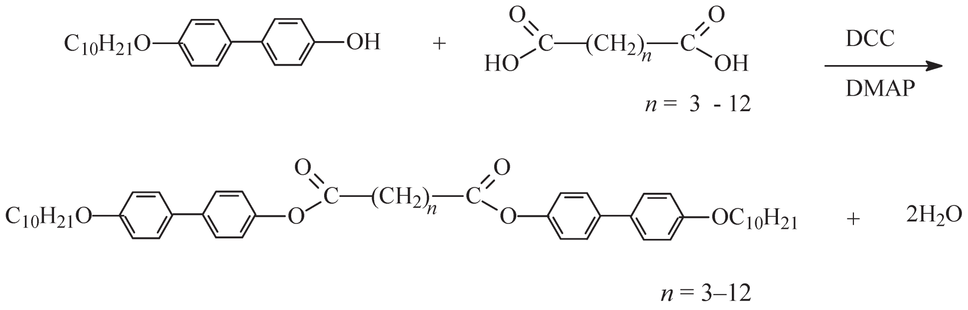
Typical characterisation results are given below for esters of octanedicarboxylic acid (n=8) and undecanedicarboxylic acid (n=11).

For n=8, FT-IR (cm^{-1}) 1751 ($C{=}O_{ester}$). ^{1}H NMR (ppm) 0.88 (t, 6H, 2× CH_3), 1.23–1.89 (m, 36H, 2× $(CH_2)_9$ and 8H $(CH_2)_4$), 2.58 (t, 4H, $-CH_2COO-$), 3.99 (t, 4H, $-CH_2O-$), 6.93–7.55 (m, 16H, C_{ar}–H.). Yield 54%.

For n=11, FT-IR (cm^{-1}) 1750 ($C{=}O_{ester}$). ^{1}H NMR (ppm) 0.88 (t, 6H, 2× CH_3), 1.22–1.83 (m,



Scheme 1. Structure of the symmetrical dimers studied.



Scheme 2. General route employed for synthesis of symmetrical dimers.

Table 1. The liquid crystalline properties of 4-decyloxy-4′-hydroxybiphenyl esters of α,ω-alkanedicarboxylic acids as a function of the methylene unit, *n*, in the spacer.

n	Phase transition temperatures/°C, enthalpies (in parentheses)/kJ mol^{-1}	*d*/nm	*l*/nm	*d*/*l*
3	G 145.3 (5.78) B4 187.9 (55.81) I	4.6	4.6	1.0
4	Cr 157.9 (26.48) SmX 191.8 (11.96) SmC 204.37 (26.43) I	4.4	5.3	0.83
5	Cr_1 153.6 (14.56) Cr_2 163.8 (56.24) I	–	–	–
6	Cr 145.3 (31.36) SmX 180.3 (29.27) I	4.6	5.5	0.84
7	G 118.7 (0.83) B4 158.5 (73.05) I	5.1	4.8	1.06
8	Cr 147.3 (33.37) SmX 173.3 (43.60) I	4.3	5.6	0.77
9	G 117.2 (1.38) B4 156.5 (76.69) I	5.4	5.4	1.0
10	Cr 151.5 (34.96) SmX 165.29 (46.70) I	4.7	6.0	0.78
11	G 126.2 (1.18) B4 153.6 (84.12) I	5.8	5.5	1.05
12	Cr 150.6 (22.14) SmX 157.6 (47.97) I	5.1	6.2	0.82

36H, 2× $(CH_2)_9$ and 14H $(CH_2)_7$), 2.57 (t, 4H, $–CH_2COO–$), 3.99 (t, 4H, $–CH_2O–$), 6.93–7.55 (m, 16H, C_{ar}–H.). Yield 48%.

3. Results and discussion

The LC properties of the synthesized compounds are collected in Table 1. Transition temperatures were taken from DSC traces and correspond to the onset points of the enthalpy peaks.

The thermal characteristics of the compounds with odd and even number of carbon atoms in the methylene spacer essentially differ. The dependence of the isotropization temperatures and clearing entropy changes on the number of methylene units in the spacer, shown in Figure 1, reveals strong odd–even effect.

Compounds with an even number of atoms in the methylene spacer have higher clearing temperatures than those with an odd number. The alternation attenuates with increasing spacer length. The clearing transition entropy changes for compounds with an odd number of the methylene units are nearly twice as large as those with even number and do not decrease with increase of the spacer length. Such behaviour is rather uncommon; usually dimers with higher clearing temperatures are also characterised by higher

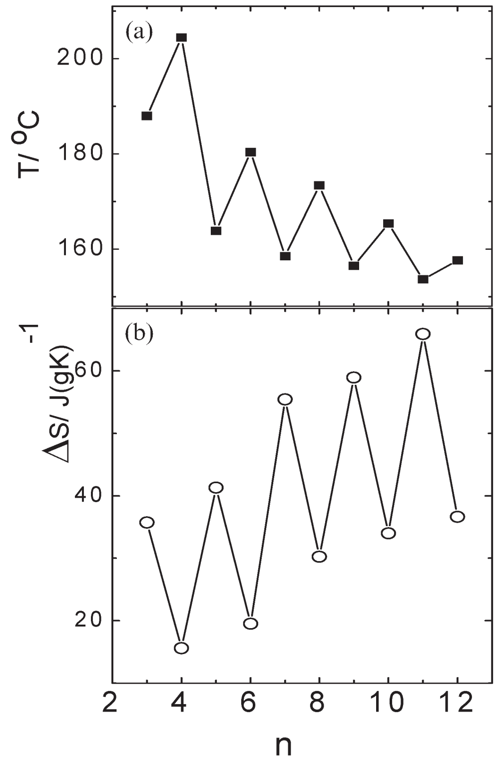


Figure 1. The dependence of the isotropization temperatures (a) and clearing entropy changes (b) on the number of methylene groups, *n*, in the spacer.

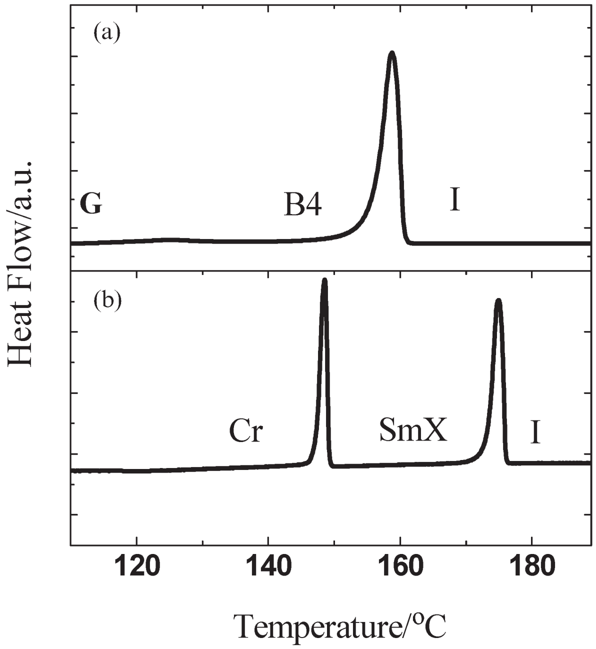


Figure 2. DSC thermograms taken in heating scan for compounds: (a) with $n=9$ and (b) with $n=8$.

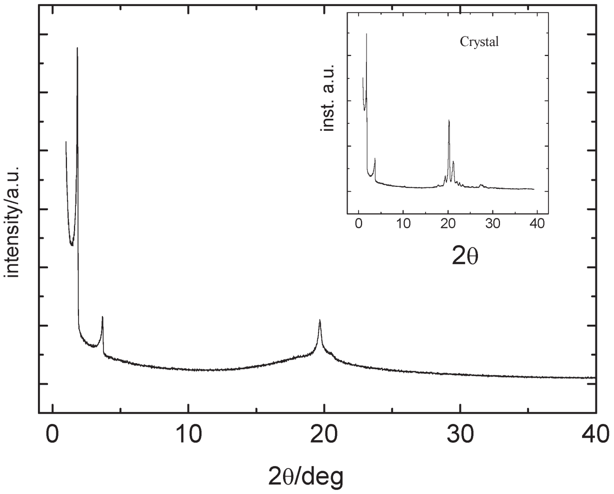


Figure 3. X-ray diffraction pattern as a function of 2θ angle for the compound with $n=8$ taken at 150°C in B4 phase. Inset: the X-ray pattern in the crystal phase taken at room temperature.

clearing entropies (*1*). Additionally, in the case of compounds with an odd number of carbon atoms in the spacer we observed the glass transition before the LC phase, whereas the smectic phase follows the crystalline one for compounds with an even-numbered spacer (Figure 2).

The X-ray diffraction patterns of compounds with an even number of methylene units in the spacer ($n=4$, 6, 8, 10, 12) revealed rather sharp signal in the wide-angle region and single sharp signal (and its second harmonic) in the small-angle region (see, for example, Figure 3). The pattern suggests crystalline-type smectic G or J phases. The smectic layer spacing, *d*, is considerably smaller than the molecule length, *l*, calculated for the most extended conformations. The measured layer spacing, together with microscopic observation (Figure 4), indicates that the molecules are tilted from the layer normal by an angle of 33–45 deg.

The tilt angle for smectic X (SmX) phases does not change with temperature. For the compound with $n=4$, above the crystalline smectic phase, a tilted liquid-like smectic C (SmC) phase also appears, with slightly smaller layer thickness than in the crystalline phase. The increase in the layer spacing indicates stretching of the molecular conformation at the LC phase transition (Figure 5). Neither SmC nor SmX phase was switchable in an electric field.

POM observations of the compounds with odd number of methylene units in the spacer ($n=3$, 7, 9, 11) performed on slow cooling from the isotropic phase reveal large weakly birefringent domains characteristic for the B4 phase. Two domains with opposite optical activity can be distinguished by decrossing polarisers (see Figures 6 (a) and 6 (b)).

A characteristic blue colour of scattered light is also observed for these samples. The X-ray pattern of B4 phase showed several harmonics of

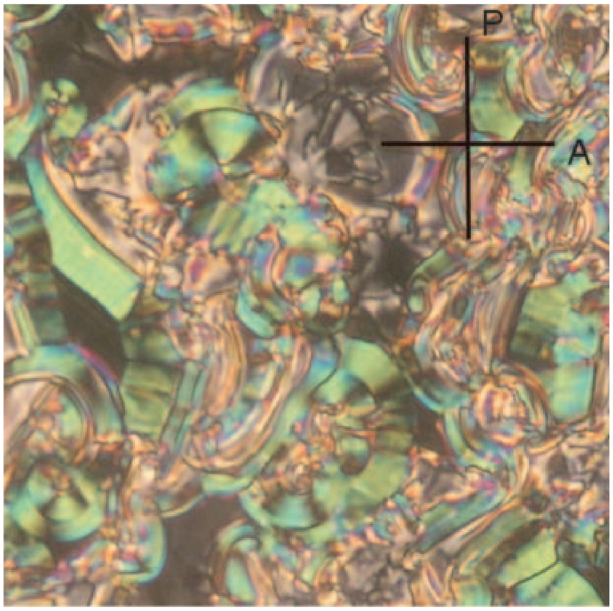


Figure 4. Texture of the SmX phase of the dimer with $n=8$ at 157°C after cooling from the isotropic phase. Arrows indicate the polariser directions. The extinction light directions in circular domains are inclined from the polariser-analyser direction by ~45 deg, indicating the tilted smectic phase.

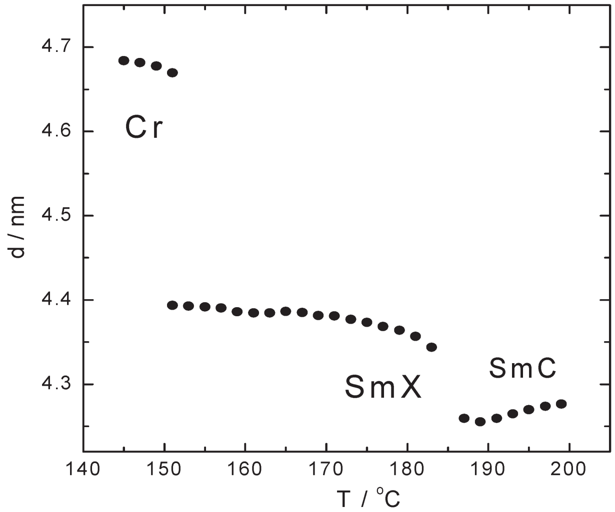


Figure 5. Temperature dependence of the layer thickness, *d*, for compound with $n=4$.

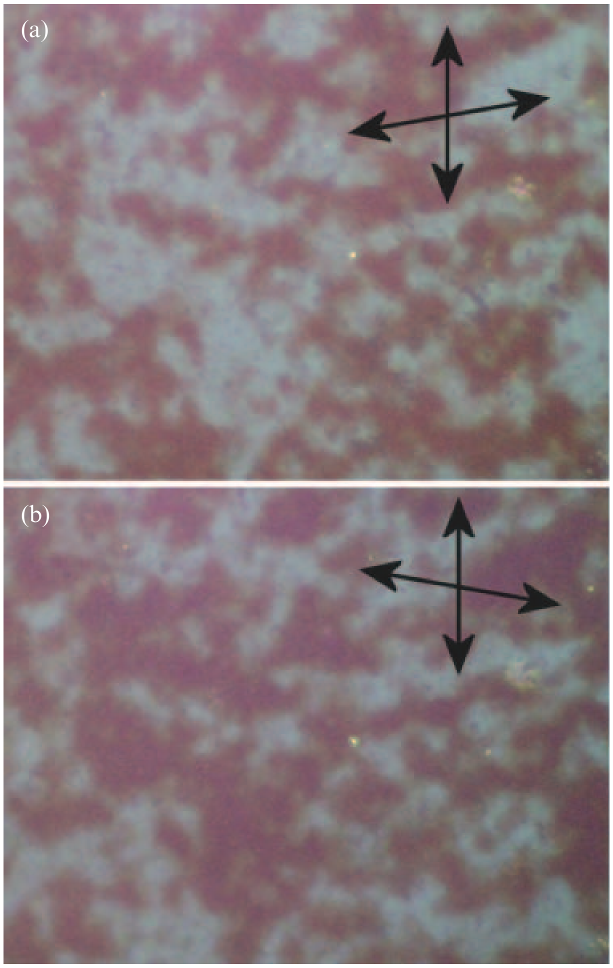


Figure 6. Optical micrographs of the B4 phase of the compound with $n=7$ at 152°C obtained upon cooling from the isotropic phase: (a) and (b) textures observed by 5 deg decrossing of polarisers clockwise and anticlockwise, respectively.

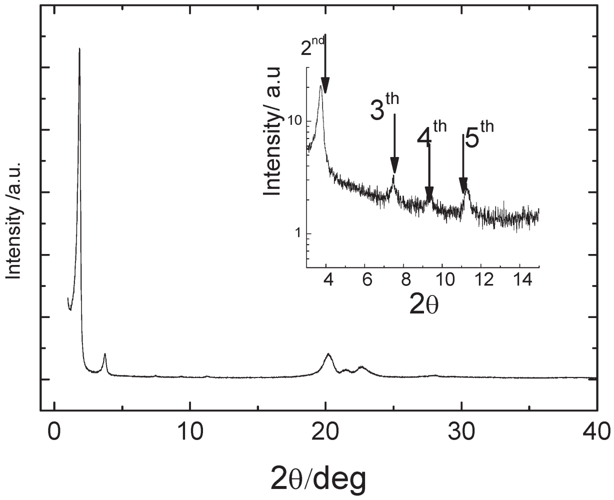


Figure 7. X-ray diffraction pattern as a function of 2θ angle for the compound with $n=3$ taken at 165°C in the SmX phase. Inset: enlarged fragment of the scan showing several harmonics of the main 'layer' signal.

the signal corresponding to the main 'layer' periodicity (Figure 7).

This suggests that the electron density distribution along the layer normal is very different to that in the SmX phase; the layers have sharp boundaries, suggesting weak interdigitation of molecules between the layers. However, comparing the broadness of the 'layer signal' it can be noticed that in the B4 phase the peak has nearly twice the width of signal in the SmX phase (Figure 8). The broadening of X-ray signals is a well known effect related to grain size. Estimated from the Debey–Scherrer formula, on the basis of the full width of the peak at half-maximum height, the grain size in the B4 phase is about 120–150 nm. Such finite size blocks, arranged helicoidally, are consistent with recently proposed model of the B4 phase (*15*). The position of the signal implies that the molecules are non-tilted in the blocks.

The in-plane smectic structure is characterised by long-range order, as indicated by the few sharp reflections observed in the wide-angle region; however, no signals showing correlations between the layers were observed. The B4 phase exhibits no electric field-induced molecular reorientation and low dielectric response. When comparing the length of the molecules for the most stable geometry (obtained using Hyperchem 6 package; see inset in Figure 8), the B4 phase is a non-tilted phase, whereas the SmX phase is tilted.

The compound with $n=5$ does not exhibit LC phases. The X-ray diffraction pattern shows a series of rather sharp incommensurate reflections in the wide- and small-angle ranges that indicate the crystal phase.

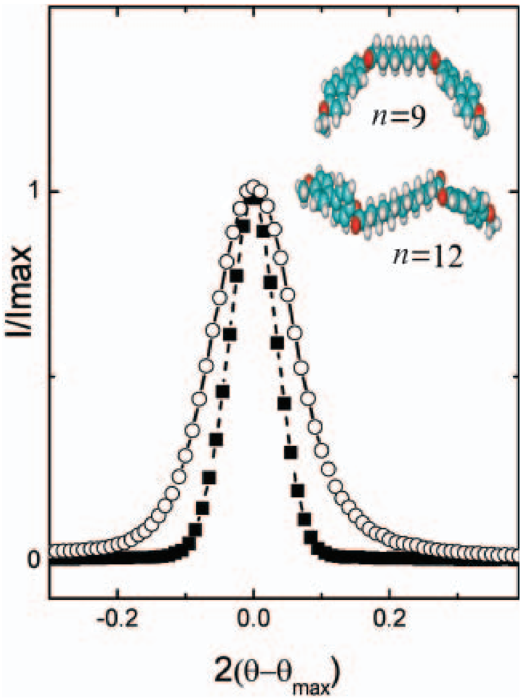


Figure 8. Bragg reflections related to the layer periodicity for the compounds with $n=9$ in B4 phase (○) and with $n=12$ in the SmX phase (■). The HWHM is 0.143 deg for the signal in B4 phase and 0.084 deg for the signal in the Sm X phase. Inset: molecular structures of relevant compounds calculated by Hyperchem 6 package. The terminal methoxy group (–OCH_3) was taken for simplicity.

4. Conclusions

The relationship between the spacer length in the dimers and the type of mesogenic phase of 4-decyloxy-4′-hydroxybiphenyl esters of α,ω-alkanedicarboxylic acids has been demonstrated. The bismesogenic molecules with even number of carbon atoms in the spacer are nearly linear and form crystalline type smectic X and liquid-like smectic C phases, whereas those with odd number of methylene groups exhibit a bent conformation and form B4 phases. The B4 phase is believed to be a unique phase for the rigid bent-core molecules.

The X-ray data show that the B4 phase has well-defined layers with sharp boundaries and long-range, in-plane order. The stronger layered character of the B4 phase than that of the SmX one is probably responsible for larger thermal effects at the liquid crystal–isotropic phase transition in the case of odd-numbered homologues. The broadening of X-ray signals corresponding to the layers is consistent with the assumption that layers form blocks of finite thickness. Other characteristic features of this phase are extremely high optical activity and low birefringence.

To the best of our knowledge this is the first time that the B4 phase has been observed for dimeric LC molecules with a flexible spacer.

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