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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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New thermotropic liquid crystals derived from thiophenes

Rubing Cai^{ab}; Edward T. Samulski^a

^a Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, U.S.A. ^b

Research Center, Sherwin-Williams Company, Chicago, Illinois, U.S.A.

To cite this Article Cai, Rubing and Samulski, Edward T.(1991) 'New thermotropic liquid crystals derived from thiophenes', *Liquid Crystals*, 9: 5, 617 – 634

To link to this Article: DOI: 10.1080/02678299108030376

URL: <http://dx.doi.org/10.1080/02678299108030376>

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New thermotropic liquid crystals derived from thiophenes

by RUBING CAI† and EDWARD T. SAMULSKI*

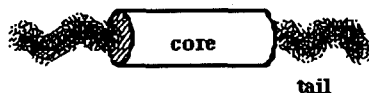
Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27599-3290, U.S.A.

(Received 18 April 1990; accepted 22 October 1990)

Properties of new homologous series of low molecular mass thermotropic liquid crystals containing non-linear mesogenic cores, 2,5-thiophene (T) and 2,2'-bithiophene (BT), are presented for the purpose of refining molecular structural prerequisites for liquid crystallinity. Herein we focus on the effect of core linearity on mesophase stability. The bis(*p*-alkoxyphenyl) dicarboxylate derivatives containing the bent T and kinked BT central units are found to form enantiotropic liquid crystal phases with nematic and smectic polymorphism, depending on the length of their terminal chains. All members of the non-linear T and BT homologous series have narrower mesomorphic temperature ranges than the corresponding compounds with linear central units (*p*-phenylene and 4,4'-biphenyl); liquid crystallinity is not found in the analogous *m*-phenylene derivatives. This finding is consonant with the established principles of prolate mesogen structural requirements, i.e. core linearity is closely related to liquid crystal phase formation and deviation from core linearity lowers mesophase stability. The results of this study indicate that the 2,5-thiophene and 2,2'-bithiophene moieties with non-linear structures are viable mesogenic core units and may be substituted for *p*-phenylene units in conventional liquid crystal molecules. Moreover, these moieties should be particularly useful for modifying the transition temperatures of liquid-crystalline polymers.

1. Introduction

There is continued interest in refining the molecular structural prerequisites for liquid crystallinity. In low molar mass liquid crystals steric interactions are dominant [1] and consequently prolate (as distinct from oblate) mesogens are anisometric with the general form



They consist of a rigid mesogenic core (usually comprised of extended 1,4-substituted aromatic rings) terminated with flexible tails (generally hydrocarbon chains). The latter facilitate the transformation from the solid state to the fluid liquid crystal phase: the flexible tails lower the melting temperature of the crystal by weakening intermolecular interactions between rigid mesogenic cores in the solid state. On heating a molecular crystal, restricted thermal motions gradually increase in amplitude up to the melting point (T_m). This may involve the population of rotational isomers of the flexible tails in

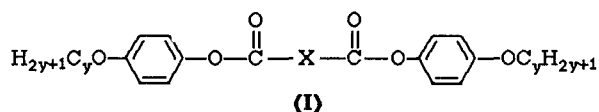
* Author for Correspondence.

† Present Address: Research Center, Sherwin-Williams Company, 10909 S. Cottage Grove Avenue, Chicago, Illinois 60471, U.S.A.

the mesogen and/or transformation of mesogen packing in the crystal. At T_m there is an abrupt collapse of the long range translational and orientational order and in the resulting fluid phase the rapidly isomerizing molecules interact with one another via motionally averaged intermolecular forces. In fluids composed of anisometric molecules with large (average) aspect ratios, local packing considerations may result in effective, anisotropic dispersion forces [2]. In such cases a delicate balance between the residual anisotropy of these forces and the thermal energy sometimes yields a range of temperature wherein long range orientational order persists in the fluid. Such long range molecular orientational order in a fluid is the signature of the nematic phase.

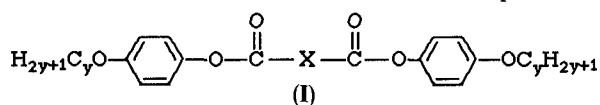
In a large number of homologous series, the flexible tails also play another role in mesomorphism. When the hydrocarbon chain length exceeds some value (~ 5 carbons), varying degrees of translational order may be superimposed on the orientational order. The resulting stratification in liquid crystal fluids is probably driven by a combination of factors (e.g. chemical differences between the core and the chain as well as local entropic/packing considerations of the tails) leading to *nano*-aggregation; the flexible tails segregate from the cores, each defining a separate layer in the fluid. Such translationally ordered fluids are called smectic phases.

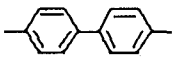
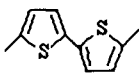



Clearly, mesogen shape anisotropy and terminal chain length are key variables in strategies to design new mesogens exhibiting specific types of molecular organization in a particular range of temperature [3]. Here we focus on mesogen shape cognizant that the usual starting point for constructing a new mesogen is a linear mesogenic core composed of a variety of (typically aromatic) molecular subunits. There are many examples of rigid, extended chemical subunits in mesogens, but by far the most common one is the linear *para*-substituted phenylene ring; this subunit is a component of most of the known liquid crystals [4, 5]. In view of the general requirements for liquid crystallinity, it would appear that the non-linear *meta*-substituted phenylene ring is antithetical to liquid crystal stability. In fact, a perusal of the literature [4, 5] shows that the non-linear geometry of the *m*-phenylene ring (120° core angle) is not conducive to liquid crystal formation. Herein we consider more closely core linearity as a molecular structural prerequisite for liquid crystallinity. Namely, we investigate how much deviation from core linearity can be tolerated in a mesogenic molecule. In order to study this aspect of core molecular structure on liquid crystal stability, we consider several homologous series of symmetric model compounds (I) wherein different central



units (X) may be incorporated into the mesogenic core of potential liquid crystal molecules. It is our goal to examine core linearity within a series of X units wherein geometry is the primary variable. The specific X units and the corresponding core angles with which we are concerned in this report are shown in table 1. They include three new homologous series with X = 2,5-thiophene (T), X = 2,2'-bithiophene (BT) and X = 4,4'-biphenyl (BP). We have also synthesized the homologous series with X = *p*-phenylene (PP) in the context of comparisons with these series and a re-examination of the literature reports on the PP series where we conclude that previous phase assignments are incorrect. Thus, we contrast the properties of the X = T derivatives with X = PP and X = *m*-phenylene (MP) compounds, and the X = BT derivatives with their BP counterparts. We employ the X = T (and BT) unit as a non-linear central unit

Table 1. Molecular structures of model compounds.



X (abbreviation)	Molecular structure	Core angle
4,4'-Biphenyl (BP)		Linear (180°)
2,2'-Bithiophene-5,5'-(BT)		Not collinear (parallel)
<i>p</i> -Phenylene (PP)		180°
2,5-Thiophene (T)		148°
<i>m</i> -Phenylene (MP)		120°

in an examination of the role of core geometry in structure/property relationships within the progression from the linear core X=PP (and BP) to the bent core MP. Moreover, we are reasonably sure that we are primarily studying geometric phenomena associated with core geometry; the aromaticity and chemistry of thiophene derivatives are quite similar to their phenylene analogues [6]. Hence, for all practical purposes, the T unit merely introduces a $\sim 30^\circ$ bend (and BT, a kink) into the mesogen shape.

2. Experimental

2.1. Synthesis

All series (I) compounds (except biphenyl derivatives) were synthesized from diacid chlorides of the X unit and *p*-alkoxyphenols. 2,5-Thiophenedicarbonyl chloride was prepared from the diacid (Chem Service) with thionyl chloride catalysed by DMF, and 2,2-bithiophene-5,5'-dicarbonyl dichloride was prepared from 2,2'-bithiophene by the method of Barber and Maxwell [7]. 4,4'-Biphenyldicarboxylic acid, terephthaloyl dichloride and isophthaloyl dichloride are commercial products (Aldrich). *p*-*n*-Octyloxyphenol, *p*-*n*-nonyloxyphenol and *p*-*n*-decyloxyphenol were synthesized according to the procedures described in [8], and the remaining *p*-*n*-alkoxyphenols were obtained from commercial sources (Aldrich and TCI). DCC esterification [9] was used to prepare the model compounds with X = 4,4'-biphenyl.

A typical example of a synthesis (X = BT) is as follows. A solution of *p*-alkoxyphenol (1.2×10^{-5} mol) and 2,2'-bithiophene-5,5'-dicarbonyl dichloride (5×10^{-6} mol) in chloroform with a small amount of pyridine was stirred for 20 hours at 60°C (the PP, T and MP series were synthesized in dichloromethane solution at 40°C). The solvent was removed by rotary evaporation and the residue was dissolved in chloroform. The solution was acidified with dilute hydrochloric acid and extracted with chloroform.

After washing the chloroform fraction with alkaline water and water, the product was recrystallized from either chloroform (bithiophene series) or ethyl acetate (thiophene series). The purity was checked by thin-layer chromatography and the presence of a constant, sharp transition in differential scanning calorimetry traces.

2.2. Characterization

High resolution mass spectroscopy was used to confirm the atomic composition of all the compounds; measured molecular weights agree with those calculated to within 5 ppm. The phase transition temperatures and associated thermodynamic parameters were determined from DSC measurements using a Perkin-Elmer DSC-4. The phase diagrams were constructed from the transition temperatures obtained from the DSC heating traces. The mesophases were identified with a Nikon (Microphot-FX) polarizing microscope equipped with a Linkam (TMS-90) hot stage.

Table 2. Thermodynamic properties of bis(*p*-alkoxyphenyl) 2,2'-bithiophene-5,5'-dicarboxylates (BTy) (on heating).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{mol}^{-1}$
BTH†	C-I	186.4	43.1	93.8
BT1	C-N	246.2	57.6	110.8
	N-I	283.1	1.1	2.0
BT2	C-N	218.4	47.4	96.5
	N-I	282.1	1.2	2.1
BT3	C-S _A	199.9	43.7	92.4
	S _A -N	215.2	0.7	1.4
	N-I	252.7	1.1	2.2
BT4	C-C	106.2	13.2	34.7
	C-S _A	170.6	30.6	69.1
	S-N	232.6	1.3	2.5
	N-I	250.1	1.0	2.0
BT5	C-C	99.6	2.0	5.4
	C-C	105.7	5.2	13.8
	C-C	130.2	2.4	6.0
	C-S _C	149.6	29.6	70.1
	S _C -S _A ‡	188.0	—	—
	S _A -N	231.4	1.8	3.7
BT6	N-I	236.8	1.3	2.6
	C-C	111.1	3.8	9.9
	C-C	125.6	6.9	17.3
	C-S _C	139.8	22.5	54.5
	S _C -S _A ‡	211.0	—	—
	S _A -N	232.6	3.7	7.3
BT7	N-I	234.1	2.3	4.5
	C-C	116.0	9.8	25.2
	C-C	127.7	14.6	36.4
	C-S _C	137.7	24.6	59.9
	S _C -S _A ‡	219.0	—	—
S _A -I	224.8	7.1	14.2	

† Diphenyl 2,2'-bithiophene-5,5'-dicarboxylate.

‡ Transition temperature observed by optical microscopy.

3. Results

We first consider the series of model compounds with $X = 2,2'$ -bithiophene (BTy; y is the number of carbon atoms in the alkyl chain tail) and compare their transitional properties with those of the biphenyl analogues (BPy). Thermodynamic data for the BTy series are summarized in table 2 and figure 1. The compound with no alkoxy tails, BTH (diphenyl 2,2'-bithiophene-5,5'-dicarboxylate), is not liquid crystalline but both BT1 and BT2 show nematic phases. A smectic A phase appears in the BTy series when $y > 2$; these mesogens display a typical focal conic fan texture. Compounds BT5, BT6 and BT7 show a S_C phase as well as a S_A phase. (For alkyl terminal chains containing four and higher numbers of carbons, this series shows solid state transitions before the melting transition).

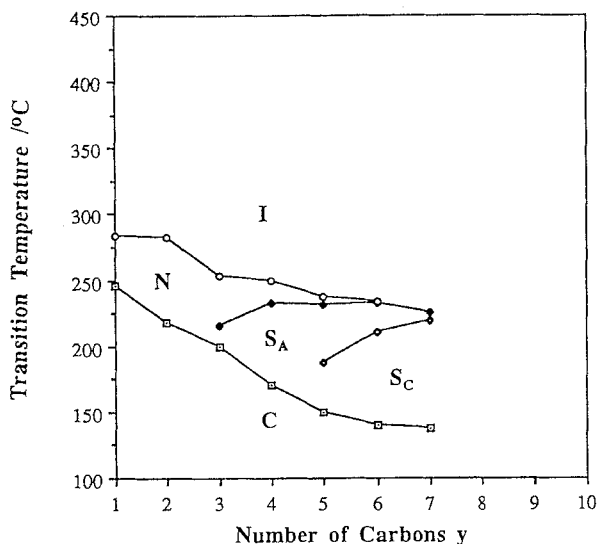


Figure 1. Transition temperatures versus the number of carbons for the 2,2'-bithiophene-5,5'-dicarboxylate (BTy) series. Abbreviations: C, crystal; S_C , smectic C; S_A , smectic A; N, nematic; I, isotropic liquid. The open squares indicate the melting transition; the open circles indicate the N-I transition; the solid diamonds indicate the S_A -N transition; the open diamonds indicate the S_C - S_A transition.

Plate 1. Bis(*p*-pentyloxyphenyl) 2,2'-bithiophene-5,5'-dicarboxylate (BT5) at 190°C shows homotropic and focal conic fan textures of S_A phase; crossed polars and 100×.

Plate 2. Bis(*p*-pentyloxyphenyl) 2,2'-bithiophene-5,5'-dicarboxylate (BT5) at 150°C shows schlieren and broken focal conic fan textures of S_C phase; crossed polars and 100×.

Plate 3. Bis(*p*-heptyloxyphenyl) 2,5-thiophenedicarboxylate (T7) at 135°C shows a schlieren nematic texture; crossed polars and 200×.

Plate 4. Bis(*p*-heptyloxyphenyl) 2,5-thiophenedicarboxylate (T7) at 128°C shows a S_C texture; crossed polars and 100×.

Plate 5. Bis(*p*-heptyloxyphenyl) terephthalate (PP7) at 179°C shows a homotropic and focal conic fan textures of S_A phase; crossed polars and 100×.

Plate 6. Bis(*p*-heptyloxyphenyl) terephthalate (PP7) at 172°C shows schlieren and broken focal conic fan textures of the S_C phase; crossed polars and 100×.

Plate 1.



Plate 2.

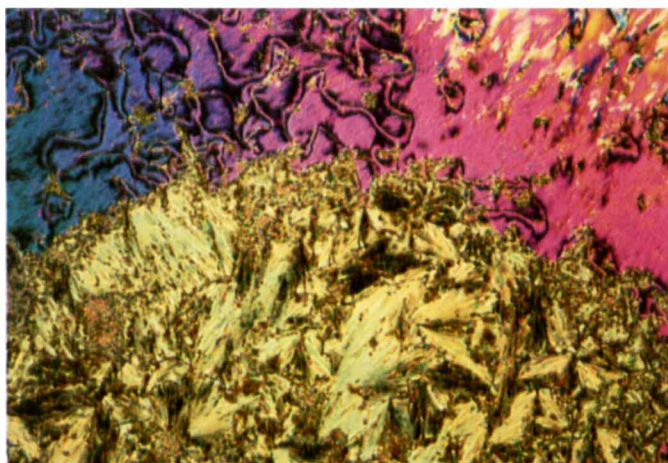


Plate 3.

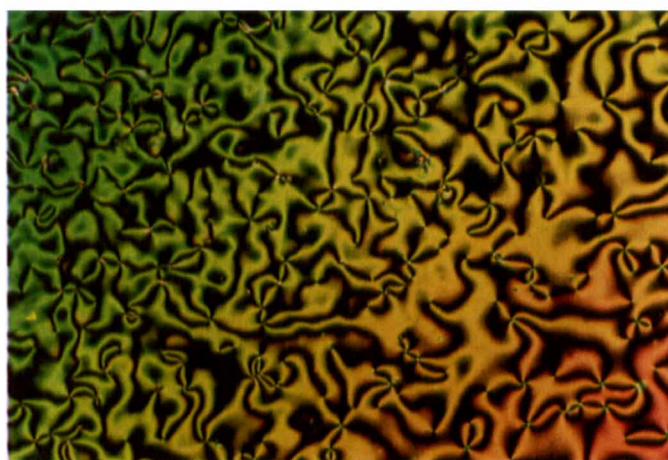


Plate 4

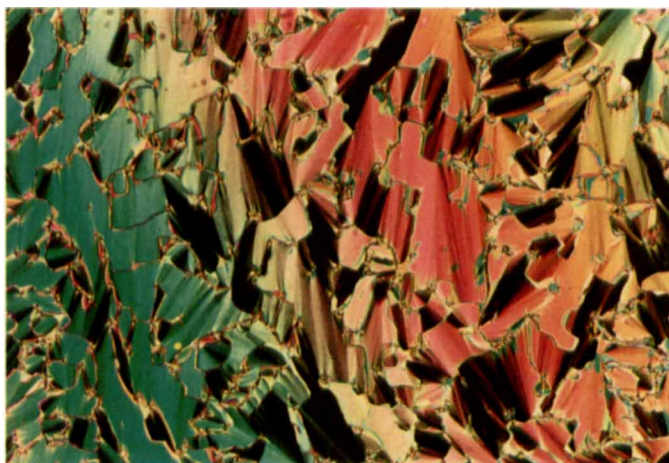


Plate 5.

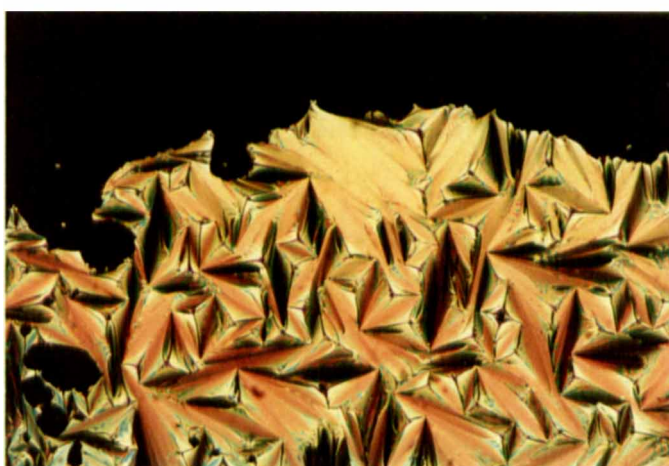
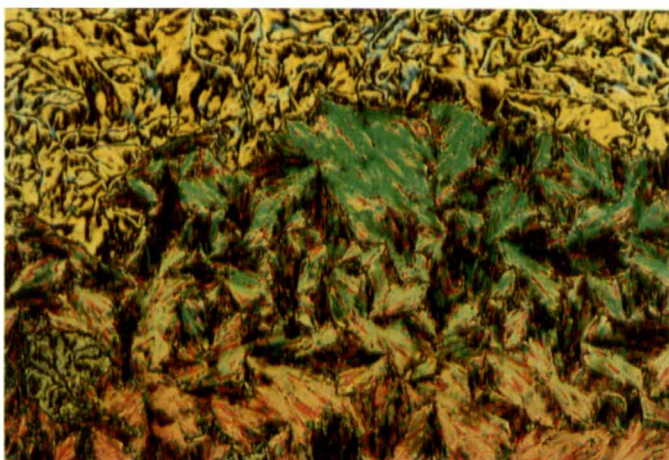


Plate 6.



The phase assignments were made with polarizing optical microscopy. Plates 1 and 2 show photomicrographs of the S_A and S_C phases of BT5, respectively. In Plate 1, the dark region corresponds to a homotropically aligned S_A that coexists with the focal conic texture just above the S_A - S_C transition (188°C). When the sample is cooled below the S_A - S_C transition, plate 2 shows that the dark region of plate 1 is transformed into a schlieren texture. Simultaneously, the focal conic region (plate 1) is transformed into a broken focal conic fan texture (plate 2), characteristic of the S_C phase [10]. With increasing carbon number y , the S_A phase expands at the expense of the nematic phase. In turn, the S_A phase is crowded out by the S_C phase at higher y values. The melting temperature decreases more rapidly than the clearing temperature with increasing tail length, hence, the overall range of mesomorphism increases as y increases.

Thermodynamic data for the 4,4'-biphenyl (BP y) compounds are given in table 3 and figure 2. BPH (diphenyl 4,4'-biphenyldicarboxylate) shows a nematic phase whereas its analogue BTH is not a liquid crystal. S_A and nematic phases are observed for the entire BP y homologous series (BP2 was not synthesized). Both BP6 and BP7

Table 3. Thermodynamic properties of bis(*p*-alkoxyphenyl)4,4'-biphenyl-dicarboxylates (BP y) (on heating).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
BPH†	C-C	179.8	4.8	10.5
	C-N	211.8	38.4	79.1
	N-I	245.4	0.5	0.9
BP1	C-C	182.4	3.3	7.2
	C- S_A	193.1	28.7	61.6
	S_A -N	231.3	0.03	0.06
	N-I	>400	—	—
BP3	C- S_A	194.9	45.7	0.7
	S_A -N	325.1	97.7	1.2
	N-I	>400	—	—
BP4	C- S_A	171.2	34.2	77.0
	S_A -N	339.6	1.6	2.6
	N-I	366.5	2.4	3.8
BP5	C-C	105.4	19.4	50.2
	C- S_A	145.4	30.6	73.1
	S_A -N	335.4	2.7	4.4
	N-I	346.0	2.1	3.4
BP6	C-C	102.2	18.2	48.5
	C- S_C	139.3	31.2	75.6
	S_C - S_A ‡	160.0	—	—
	S_A -N	329.2	4.5	7.5
	N-I	332.6	2.5	4.1
BP7	C-C	115.6	28.4	73.1
	C- S_C	139.4	29.6	71.9
	S_C - S_A	211.0	0.8	0.2
	S_A -N	318.2	2.6	4.4
	N-I	319.5	4.7	7.9

† Diphenyl 4,4'-biphenyldicarboxylate.

‡ Transition temperature observed by optical microscopy.

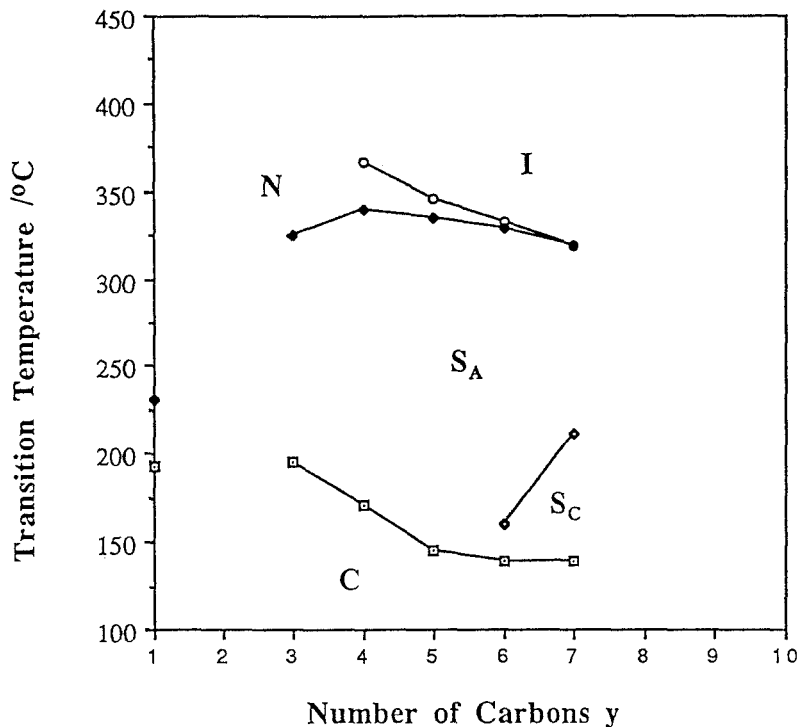


Figure 2. Transition temperatures versus the number of carbons for the 4,4'-biphenyldicarboxylate (BPy) series. Abbreviations: C, crystal; S_C, smectic C; S_A, smectic A; N, nematic; I, isotropic liquid. The open squares indicate the melting transition; the open circles indicate the N-I transition; the solid diamonds indicate the S_A-N transition; the open diamonds indicate the S_C-S_A transition.

show S_C phases also. The nematic-isotropic transition temperatures for BP1 and BP3 are higher than the decomposition temperatures ($\sim 400^\circ\text{C}$), and the overall mesophase range for the BP series is much wider than that of the BT series.

Thermodynamic data for 2,5-thiophene derivatives (Ty) are summarized in table 4 (heating) and table 5 (cooling). The transition temperatures from table 4 are plotted in figure 3 on the same scale as the BPy and BTy series to emphasize the decrease in mesophase stability caused by the introduction of non-linearity into the mesogenic core. The compound TH (diphenyl 2,5-thiophenedicarboxylate) is not liquid-crystalline. However, contrary to earlier reports [11, 12], bis(*p*-methoxyphenyl) 2,5-thiophene dicarboxylate (T1) does show an enantiotropic phase. The narrow mesophase range in compound T1 is only observed at very low DSC heating rates ($< 2^\circ\text{C}/\text{min}$). This phase is identified as a nematic by optical microscopy. Except for T3 and T4, compounds T1-T7 in this series form enantiotropic nematic phases. For T7, in addition to the enantiotropic nematic phase (plate 3), a monotropic smectic phase is also observed on cooling (plate 4). We infer this to be a S_C phase because enantiotropic S_C phases are exhibited for the higher homologues of this series. However, since the Ty series has no S_A phase, we could not identify the S_C phase in the higher homologues ($y > 7$) solely by texture examination as in the case of the BYy series. Therefore, we used miscibility studies to confirm the identity of the S_C phase [13]. The

Table 4. Thermodynamic properties of bis(*p*-alkoxyphenyl) 2,5-thiophene-dicarboxylates (Ty) (on heating).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{mol}^{-1}$
TH†	C-I	133.9	38.4	94.3
T1	C-N	164.2	30.1	68.7
	N-I	166.2	—‡	—
T2	C-N	163.4	43.2	98.9
	N-I	180.1	1.0	2.2
T3	C-I§	158.9	31.7	73.4
T4	C-C	90.9	11.1	30.6
	C-I§	157.1	45.4	105.6
T5	C-C	91.9	13.7	73.5
	C-N	136.6	43.1	105.2
	N-I	140.7	0.8	1.8
T6	C-C	106.0	11.2	29.5
	C-N	129.8	40.0	99.3
	N-I	143.6	1.0	2.4
T7	C-C	115.7	12.3	31.6
	C-C	122.3	7.6	19.2
	C-N	130.7	39.7	98.3
	N-I	135.7	1.4	3.4
T8	C-C	117.4	13.1	33.6
	K-S _c	123.9	44.6	112.3
	S _c -N	135.5	3.3	8.3
	N-I	138.2	2.5	6.0
T9	C-C	120.6	8.6	21.8
	C-S _c	126.5	60.6	151.7
	S _c -I	136.4	9.1	22.3
T10	C-C	118.3	11.4	29.1
	C-S _c	124.4	60.4	151.9
	S _c -I	137.3	10.6	25.9

† Diphenyl 2,5-thiophenedicarboxylate.

‡ Peaks overlap in DSC trace.

§ Monotropic liquid crystal.

Table 5. Thermodynamic properties of bis(*p*-alkoxyphenyl) 2,5-thiophene-dicarboxylates (Ty) (on cooling).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{mol}^{-1}$
TH†	I-C	117.0	24.7	63.4
T1	I-N	164.9	0.4	1.0
	N-C	142.7	22.3	53.6
T2	I-N	179.8	1.1	2.4
	N-C	142.2	30.6	74.7
T3	I-N	155.2	0.3	0.6
	N-C	153.4	29.9	70.2
T4	I-N	152.7	1.0	2.3
	N-C	143.9	34.8	83.6
T5	I-N	140.7	0.7	1.6
	N-C	128.8	41.9	104.3
T6	I-N	143.4	1.2	3.0
	N-C	123.5	37.4	94.4
T7	I-N	135.4	1.5	3.6
	N-S _C	127.2	1.3	3.4
	S _C -C	124.7	36.9	92.7
T8	I-N	137.6	2.8	6.8
	N-S _C	134.8	3.0	7.3
	S _C -C	121.3	43.2	109.6
T9	I-S _C	135.7	9.3	22.8
	S _C -C	122.8	62.3	157.5
T10	I-S _C	136.2	10.7	26.2
	S _C -C	121.3	43.2	109.6

† Diphenyl 2,5-thiophenedicarboxylate.

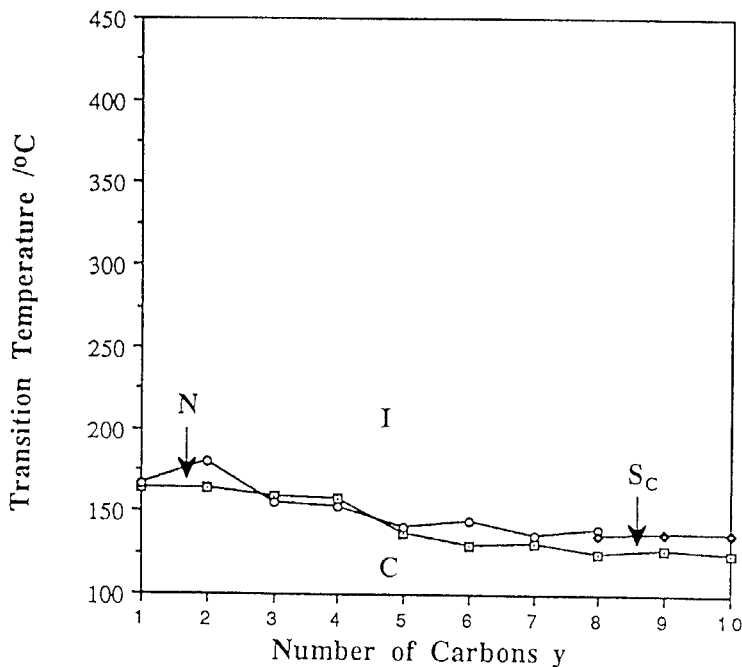


Figure 3. Transition temperatures (heating traces) versus the number of carbons for the 2,5-thiophenedicarboxylate (Ty) series. Abbreviations: C, crystal; S_C, smectic C; S_A, smectic A; N, nematic; I, isotropic liquid. The open squares indicate the melting transition; the open circles indicate the N-I transition; the solid diamonds indicate the S_A-N transition; the open diamonds indicate the S_C-S_A transition.

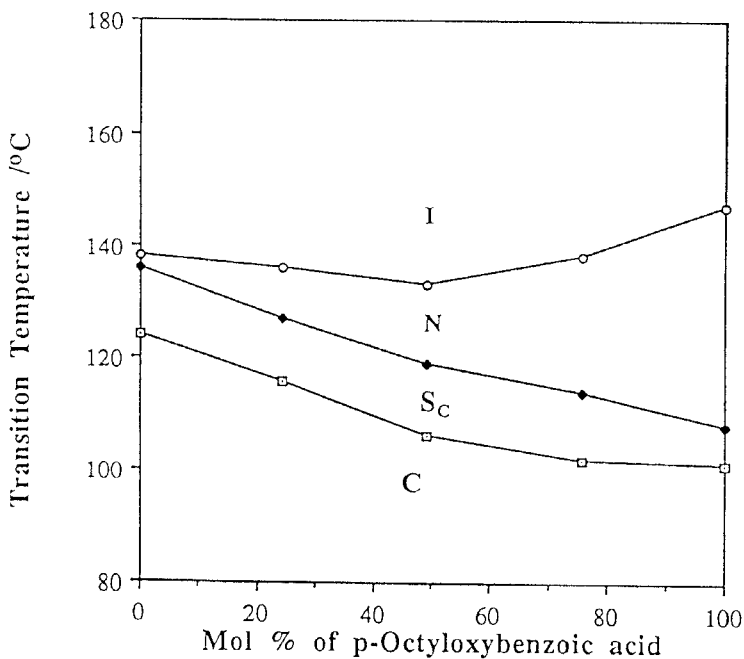


Figure 4. Phase diagram for the miscibility study of mixtures of bis(*p*-octyloxyphenyl) 2,5-thiophenedicarboxylate (T8) and *p*-octyloxybenzoic acid. Abbreviations: C, crystal; S_C, smectic C; S_A, smectic A; N, nematic; I, isotropic liquid. The open squares indicate the melting transition; the open circles indicate the N-I transition; the solid diamonds indicate the S_A-N transition; the open diamonds indicate the S_C-S_A transition.

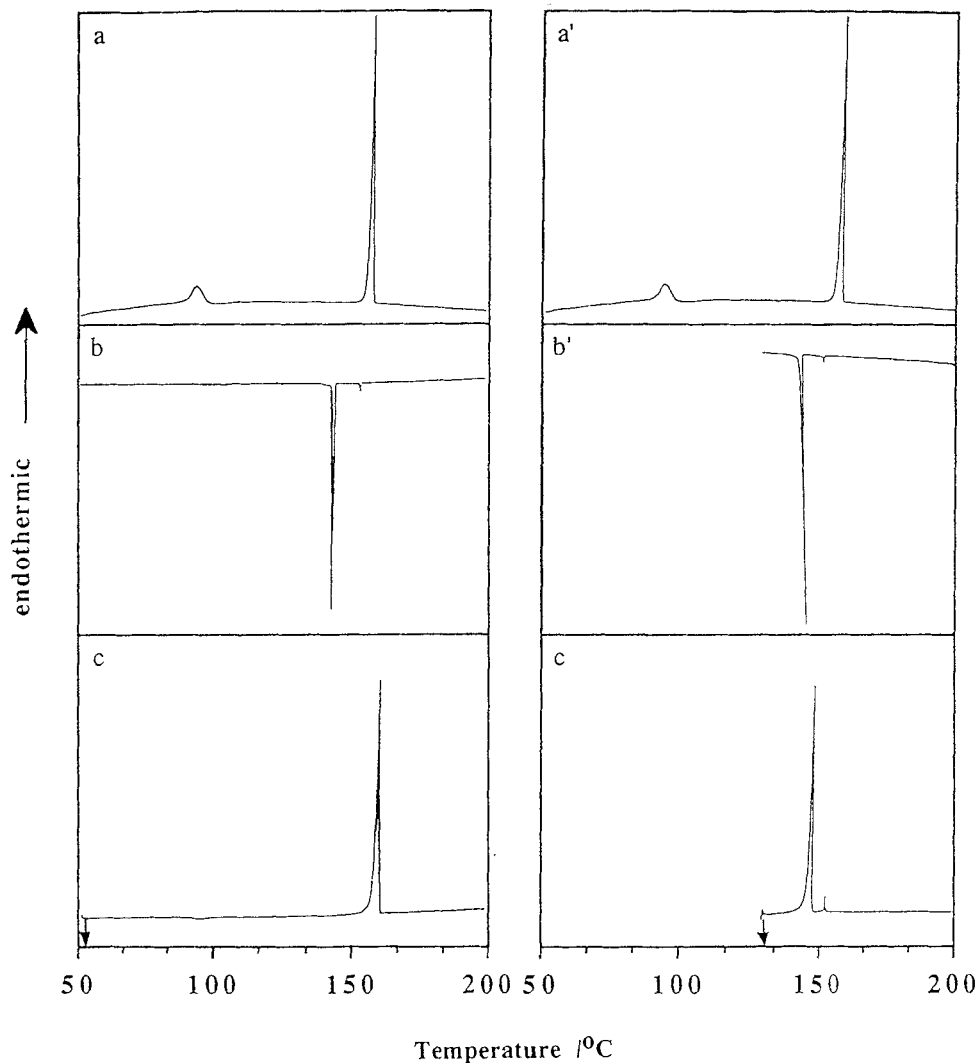
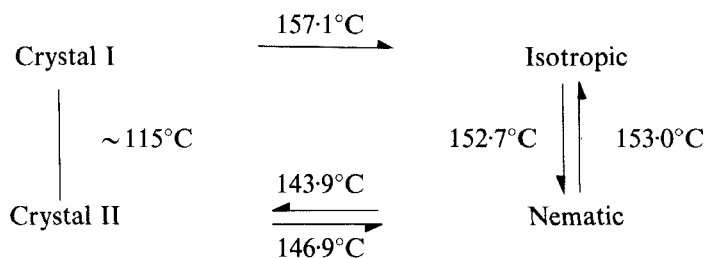


Figure 5. DSC traces of bis(*p*-butyloxyphenyl) 2,5-thiophenedicarboxylate (T4) at 5°C/min show hysteresis and a thermal history dependence: *a* and *a'* are the first heating scans, *b* and *b'* are the first cooling scans and *c* and *c'* are the second heating scans started right after the cooling scan at the temperature indicated by the arrow.

results of such a miscibility study for T8 is shown in figure 4, where we can see that T8 is miscible with a typical S_C compound, *p*-*n*-octyloxybenzoic acid, over the entire composition range.

It is noteworthy that compound T4 has a monotropic mesophase, but this transition exhibits hysteresis. In figure 5, DSC scans *a* and *a'* are the first heating scans, *b* and *b'* are the first cooling scans and *c* and *c'* are the second heating scans started right after the cooling scan. On the left hand side of the figure, the second heating scan *c* started at 50°C reproduces the first heating observations (scan *c* = scan *a*). If, however, we stop cooling the sample at any temperature between the crystallization temperature

(143.9°C) and 115°C and start the second heating from this temperature, we observe a shift to a lower melting temperature (146.9°C) and see the appearance of the nematic–isotropic transition peak at 153.0°C (scan *c'*). We can attribute this hysteresis to crystalline polymorphism:



Crystal I is stable at lower temperature and has a T_m of 157.1°C, which is above the range of mesophase stability. Crystal II forms in the cooling process and has a T_m of 146.9°C (below the T_{NI} transition). Although we were unable to detect a crystal II to crystal I transition on cooling, we infer one ($\sim 115^\circ\text{C}$) by systematically decreasing the lower limit of the interrupted cooling scans (e.g. scan *b'*). We have also verified this hysteresis phenomenon by optical microscopy and note that similar behaviour was reported for the well-known liquid crystal *p,p'*-azoxyanisole [14].

Finally, we would like to remove some errors which have been propagated in the literature about the well-known liquid crystal series **I** with $X = p$ -phenylene [15–17]. There are no problems with the lower alkyl chain numbers of this series (PP1 to PP4) which only form nematic phases. However, differences were reported for the mesophase classification for PP5, PP6 and PP7 [15–17]. Dewar and Goldberg only observed nematic phases for compounds PP6 and PP7 [15], while Verbit and Tuggey reported a smectic and a nematic phase for both PP5 and PP6 [16]. The most recent results by Cox indicated that there were two smectic phases for compounds PP5 and PP6 [17]. We have reexamined these longer alkyl chain compounds very carefully with polarizing microscopy and DSC. Our conclusions are that compounds PP6 and PP7 form S_C , S_A and nematic phases while PP5 forms S_A and nematic phases. The photomicrographs in plates 5 and 6 show clearly the S_A and S_C phases of compound PP7, which exhibit an

Table 6. Thermodynamic properties of bis(*p*-alkoxyphenyl) terephthalates (PPy) (on heating).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{mol}^{-1}$
PP5	C–C	139.8	6.7	16.4
	C– S_A	166.1	38.8	88.4
	S_A –N	173.8	0.1	0.3
	N–I	212.1	1.1	2.3
PP6	C–C	127.8	6.0	15.0
	C– S_C	160.1	38.7	89.3
	S_C – S_A	174.3	0.2	0.3
	S_A –N	180.1	0.4	0.9
	N–I	206.1	1.4	2.9
PP7	C– S_C	152.3	56.2	132.0
	S_C – S_A	176.0	0.3	0.7
	S_A –N	180.8	0.9	2.0
	N–I	194.8	1.7	3.6

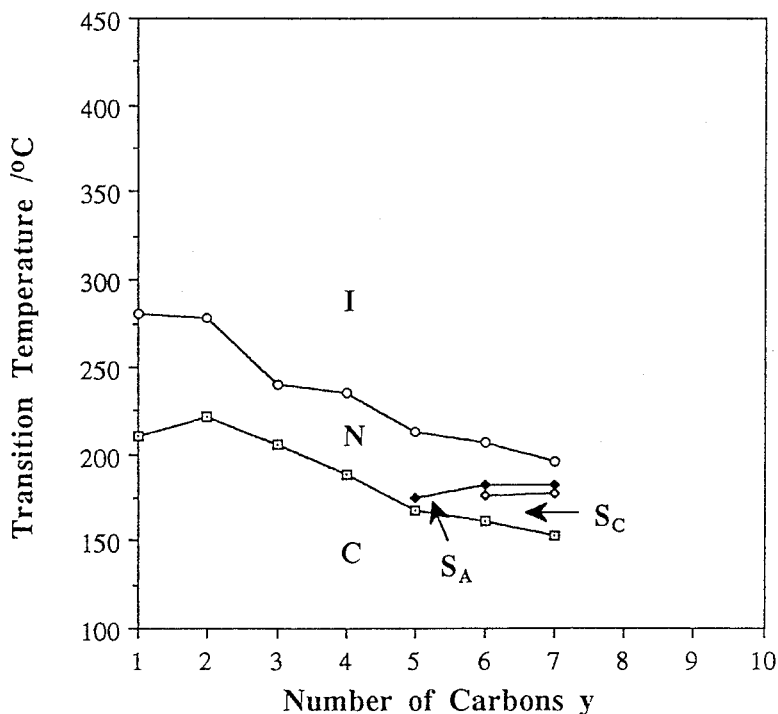


Figure 6. Transition temperatures versus the number of carbons for the terephthalate (PPy) series. The transition temperatures for PP1 to PP4 are from [16] and the transition temperatures of compounds PP5, PP6 and PP7 are from table 6. Abbreviations: C, crystal; S_C, smectic C; S_A, smectic A; N, nematic; I, isotropic liquid. The open squares indicate the melting transition; the open circles indicate the N-I transition; the solid diamonds indicate the S_A-N transition; the open diamonds indicate the S_C-S_A transition.

optical texture closely resembling those found for the corresponding smectic phases of BT5 (cf plates 1 and 2). The thermodynamic data for these compounds are given in table 6 and the corresponding phase diagram is shown in figure 6.

4. Discussion

The aim of this investigation of mesomorphism among the series of model compounds **I**, was to evaluate the effect of core geometry on liquid crystallinity, i.e. to determine if significant deviations from core linearity may be tolerated in liquid crystals. In earlier investigations along this line, bis(*p*-methoxyphenyl) 2,5-thiophenedicarboxylate (T1; compound **I** with X=T and y=1) was suggested to have a virtual liquid crystal transition (based on the extrapolation of T_{NI} in a binary mixture of this compound and a known liquid crystal [11, 12]). One member of the BP series, diphenyl 4,4'-biphenyldicarboxylate (BPH), was synthesized previously and reported to be a liquid crystal [18]. There is also some related work on the BT series: Karamysheva *et al.* reported mesomorphism in asymmetric substituted derivatives of bithiophene [19]. Before simple geometrical differences can be assessed, however, it is necessary to evaluate possible chemical differences among the various core units (X) in **I**. To this end we first review the properties of thiophene relative to those of benzene; we assume that our findings carry over to the comparisons of bithiophene with biphenyl.

It has been recognized for many years that replacing the $-\text{CH}=\text{CH}-$ moiety in aromatic hydrocarbons with the $-\text{S}-$ atom has very little effect on the physical properties of the corresponding compounds. For example, the normal boiling (melting) points of benzene and thiophene differ by less than 5° ; this also holds for a large range of derivatives of these two aromatic compounds [6]. In addition the empirical resonance energies indicate comparable magnitudes for the aromaticity of thiophene and benzene. These chemical similarities appear to carry over to the dicarboxylate derivatives considered here. For example, the melting points of dimethyl terephthalate and dimethyl 2,5-thiophenedicarboxylate are 141°C and 151°C , respectively; the diethyl analogues melt at 44°C and 52°C , respectively. These observations prompt us to ignore possible small chemical differences among the core units and focus on the geometric differences among the terephthalate, 2,5-thiophenedicarboxylate and isophthalate moieties. Similarly we may treat the 2,2'-bithiophene-5,5'-dicarboxylate unit with parallel (but not collinear) substitution [20] as a kink analogue of the 4,4'-biphenyldicarboxylate unit. We expect minimal intrinsic chemical differences between BP and BT and interpret our findings for these two series in terms of geometrical effects. (Early X-ray studies showed that the sulphur atoms are *trans* with respect to each other in 2,2'-bithiophene and that the two thiophene rings are on average coplanar [20].) In summary, the nature of the primary differences among the X units considered here are geometrical, as opposed to chemical.

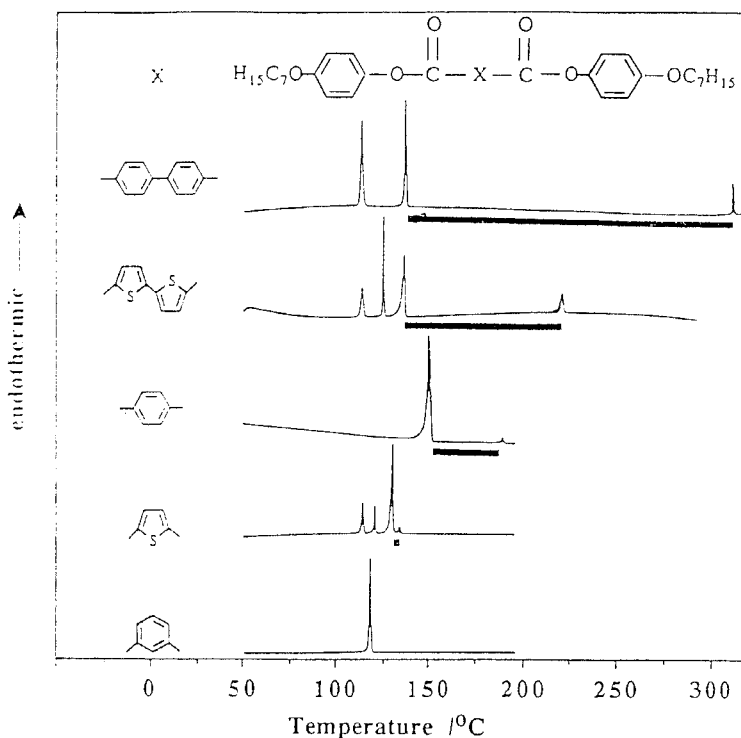


Figure 7. DSC traces of model compounds I with $\text{R} = -\text{OC}_7\text{H}_{15}$ and $\text{X} = \text{BP}$, BT , PP , T and MP (heating rate of $5^\circ/\text{min}$). The mesophase stability range is indicated by the bar below each trace. Solid state transitions are observed below the melting points for $\text{X} = \text{BP}$, BT and T .

Table 7. Thermodynamic properties of bis (*p*-alkoxyphenyl) isophthalates (MPy) (on heating).

Compound	Transition	Temperature °C	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1} \text{mol}^{-1}$
MPH†	C-I	137.4	32.8	79.8
MP1	C-I	156.3	42.2	98.3
MP7	C-I	116.9	71.9	184.3

† Diphenyl isophthalate.

Within the homologous series studied, typical behaviour is observed: the even-odd behaviour in T_{NI} is obvious, but its magnitude and the crystal melting transition decrease as the terminal chain length increases for all four series of model compounds. The BP series has the widest mesophase range; this is undoubtedly due to its large core aspect ratio (i.e. large anisotropic excluded volume interactions). It is intriguing that the BT series with a kinked core geometry shows melting temperatures which are similar to the linear BP and PP series. Similar melting points suggest that intermolecular interactions in the solid (crystal packing forces) appear to be very similar in all three series of mesogens. Hence, in so far as T_{NI} is a measure of mesophase stability, we can infer that the kink in the BT mesogen is compensated by an increase in the BT aspect ratio relative to the linear PP mesogen, and consequently, BT exhibits a higher T_{NI} than the corresponding PP mesogens. Admittedly in this comparison of PP with BT, increased anisotropic polarizability of the latter unit may contribute to the increased relative stability of the BT mesogens. It is noteworthy that related kinked mesogens, the corresponding derivatives of 2,6-naphthoic acid esters (Ny), have been synthesized [21]. There is literature data for the Ny series having $y = 1, 5-9$. For low values of y , the reported mesophase range is larger for the Ny series than the BTy series; for larger y values ($y > 6$) the melting and clearing transitions are roughly equal. However, only nematic phases are reported for the Ny series [21].

Finally, the non-linear T mesogen series shows a much narrower mesophase range than the linear PP series. All of these findings are conveniently summarized by the DSC traces of a single member of each of the series ($y = 7$). Figure 7 shows that mesophase stability as measured by the mesophase temperature range (indicated by the bar below each DSC trace) is a function of anisometry and linearity of the mesogenic core. The mesophase polymorphism changes from S_C , S_A and nematic phases in the BP compound to S_C and S_A phases in the BT compound and, from S_C , S_A and nematic phases in the PP compound, to simply nematic in the T compound; no mesophase is observed with the MP compound. The mesophase polymorphism transitions cannot be seen with the small ordinate scale of figure 7. (In addition to MP7, we also synthesized MP1 and MPH, diphenyl isophthalate, and found that none of these compounds form liquid crystal phases (see table 7).) This trend of going from a more intrinsically stable mesophase (smectic) to the less stable nematic to no mesophase is in accord with the geometrical expectations advanced by Vorlander 70 years ago [22]: deviation from core linearity lowers the mesophase stability or eliminates the mesophase altogether.

5. Concluding remarks

Bithiophene is a viable mesogenic core even though its molecular geometry causes the pendant substituents to deviate from collinearity. It is interesting that the 2,5-thiophene moiety interjecting a 148° core angle is a viable mesogenic core; homologues

exhibit enantiotropic mesophases. The narrow mesophase range observed for the 2,5-thiophene-containing model compounds indicates that within this class of mesogens, a core angle smaller than 148° should not be compatible with liquid crystallinity. Clearly the core angle in the *m*-phenylene ring (120°) is too severe for liquid crystal formation in the series of model compounds I. Based on these findings, we are convinced that the 2,5-thiophenedicarboxylic acid and 2,2'-bithiophene-5,5'-dicarboxylic acid units could be readily substituted for conventional, linear diacids in polymeric liquid crystals. In such polymers, the non-linearity and bilateral asymmetry (relative to the polymer backbone) characteristic of the thiophene monomers should perturb interchain packing and lower transition temperatures. At high contents of such non-linear monomers the result might be tractable polyesters which retain liquid-crystallinity in their melts [23].

We thank Hirokazu Toriumi for a critical evaluation of our manuscript. The research was supported by subcontracts from the University of Connecticut and the University of Pennsylvania (DARPA/ONR) Contract No. N0014-86-K-0772) and Los Alamos (DOE Subcontract 9-X59-7021-R-1).

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