Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Preliminary communication Properties of nonlinear supramolecular liquid crystals containing thiophenedicarboxylic acids

Hong-Cheu Lin; Ji-Mei Shiaw; Ri-Chen Liu; Chiitang Tsai; Hsi-Hwa Tso

Online publication date: 06 August 2010

To cite this Article Lin, Hong-Cheu , Shiaw, Ji-Mei , Liu, Ri-Chen , Tsai, Chiitang and Tso, Hsi-Hwa(1998) 'Preliminary communication Properties of nonlinear supramolecular liquid crystals containing thiophenedicarboxylic acids', Liquid Crystals, 25: 2, 277 — 283
To link to this Article: DOI: 10.1080/026782998206434
URL: http://dx.doi.org/10.1080/026782998206434

LIQUID CRYSTALS, 1998, VOL. 25, NO. 2, 277–283

Preliminary communication

Properties of nonlinear supramolecular liquid crystals containing thiophenedicarboxylic acids

by HONG-CHEU LIN*, JI-MEI SHIAW†, RI-CHEN LIU, CHIITANG TSAI† and HSI-HWA TSO*

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, Republic of China

†Institute of Applied Chemistry, Chinese Culture University, Taipei, Taiwan, Republic of China

(*Received 23 December 1997; accepted 27 January 1998*)

Novel mesogenic supramolecules have been constructed from the 2:1 molar ratio of *trans*-4-alkoxy-4′-stilbazoles C*n*PS (**1**) complexed with 2,5-thiophenedicarboxylic acid THDA (**4**) to form the kinked hydrogen-bonded (H-bonded) complexes $(C_nPS)_2$-THDA. The analogous H-bonded complexes $(C_nPP)_2$-THDA consisting of the 2:1 molar ratio of 4-alkoxypyridines C*n*PP (**2**) and THDA (**4**) are also compared. In contrast to linear complexes $(C_nPS)_2$-TA prepared from the 2:1 molar ratio of C*n*PS (**1**) and terephthalic acid TA (**5**), supramolecular liquid crystals with kinked molecular structures $(C_nPS)_2$-THDA are generated by introducing the thiophene unit into the H-bonded complexes. In addition, the chiral complex $(C5^*PS)_2$-THDA composed of an optically active proton acceptor (*S*)-(-)-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**) and THDA (**4**) (2:1 molar ratio) is reported. Significantly, the first thiophene-based supramolecular liquid crystals have been constructed in this study, and the mesogenic properties of the supramolecules can be easily adjusted not only by the nonlinear shape of the thiophene unit but also by the dipole moment derived from the lone-pair electrons of the sulphur hetero-atom.

In recent years there has been considerable interest in heterocyclic molecules due to their diversified molecular design and remarkable opto-electronic properties [1–4]. The molecular design of supramolecules has also concentrated on the utilization of heterocyclic molecules [5–7]. Significantly, recent work shows that hydrogen bonds between proton donors and acceptors can induce or promote liquid crystallinity by the supramolecular arrangement [8–12]. In these reports, heterocyclic molecules containing nitrogen hetero-atoms are the most frequently used heterocyclic fragments (hydrogen-bonded acceptors) for the assembly of liquid crystalline complexes through hydrogen bonding. Herein, we present the first thiophene-based supramolecular liquid crystals making use of non-*N*-heterocyclic structures as the H-bonding moieties.

Regarding the linearity of supramolecular liquid crystals, their most common rigid cores are linear structures with *para*-substituted aromatic rings hydrogen-bonded through pyridyl and carboxylic acid moieties. None the less, some supramolecular liquid crystals with nonlinear structures have been reported to reveal interesting mesomorphic properties, but only limited information can be obtained from the literature [13–17]. Among these publications, our most recent work shows that angular supramolecules containing different bending sites provide the ability to manipulate the mesomorphic properties of the complexes using angular hydrogen-bonded interactions [13]. In addition, Willis *et al.* [14, 15] showed that nonlinear mesogens of kinked hydrogen-bonded complexes are formed by mixing either 4-cyanophenol or 4-nitrophenol with *trans*-4-alkoxystilbazoles. Meanwhile, more linear complex structures using 3-cyanophenol (or 3-nitrophenol) instead of 4-cyanophenol (or 4-nitrophenol) revealed better mesomorphic properties. Nevertheless, the former hydrogen-bonded complexes contain only a single hydrogen bond in each system [13–15]. Recently, Willis *et al.* have reported that, after thermal annealing [17], angular hydrogen-bonded complexes containing double hydrogen bonds (formed by phthalic acid and decyloxystilbazole) showed different behaviour from unannealed complexes described in their previous publication [16]. Thus, the effects of nonlinear structures on the

*Authors for correspondence.

0267–8292/98 $12·00

mesomorphism of double H-bonded supramolecules are still vague. Consequently, in our study, instead of adjusting the relative positions of the proton donor and acceptor moieties, the five-membered heterocyclic ring (e.g. thiophene) providing the kinked molecular structure is complexed into the double hydrogen-bonded liquid crystals. Owing to the bond angles of the five-membered rings, liquid crystalline structures containing five-membered heterocyclic rings [18–23] are generally less conducive to liquid crystalline phase formation than those containing six-membered rings. However, compared with their analogous linear counterparts, the non-linear thiophene-based heterocyclic compounds [24–29] provide the benefits of lower melting temperatures and reduced packing efficiency.

As described, the first purpose of utilizing the five-membered heterocyclic proton donor (thiophene-dicarboxylic acid) is to introduce kinked molecular structure into the complexes. The other main function is to supply an extra dipole from the lone-pair electrons of the sulphur hetero-atom, whereas those of the nitrogen hetero-atom in the pyridyl group (proton acceptor) serve as the binding sites of the hydrogen bonds. The lateral dipole moment originating from the lone-pair electrons of the thiophene structure eliminates the need for lateral polar substituents which may reduce the range of mesophases. Besides, the lateral dipole within the heterocyclic structure can enhance negative dielectric anisotropy, which may avoid the disadvantage of molecular broadening and viscosity increase caused by the lateral group. Hence, it has been found that some five-membered heterocyclic rings promote the stability of the mesogenic phases as compared with 1,4-disubstituted phenyl analogues [22]. To our knowledge, there are few heterocyclic moieties containing hetero-atoms other than nitrogen in supramolecular liquid crystals, since most nitrogen hetero-atoms serve as the binding elements of the hydrogen bonds.

The hydrogen-bonded complexes (C*n*PS)$_2$-THDA and (C*n*PP)$_2$-THDA were prepared from a mixture (1:2 molar ratio) of thiophenedicarboxylic acid THDA (**4**) with *trans*-4-alkoxy-4′-stilbazoles C*n*PS (**1**) ($n = 4$, 8, 12, and 16) or with 4-alkoxypyridines C*n*PP (**2**) ($n = 8$, 12, and 16). In addition, a chiral proton acceptor, i.e. optically active (*S*)-(-)-*trans*-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**), has been synthesized and complexed with THDA (2:1 molar ratio) to form the chiral complex (C5*PS)$_2$-THDA. All hydrogen-bonded acceptor and donor moieties, including the hydrogen-bonded donor terephthalic acid TA (**5**) of their analogous linear hydrogen-bonded complexes (C*n*PS)$_2$-TA [16], are listed in figure 1. The schematic structures of angular complexes (C*n*PS)$_2$-THDA, (C*n*PP)$_2$-THDA, and linear complexes (C*n*PS)$_2$-TA are shown in figure 2. In comparison with the linear structure of (C*n*PS)$_2$-TA, the hydrogen-bonded complexes (C*n*PS)$_2$-THDA and (C*n*PP)$_2$-THDA contain 148° kinked hydrogen-bonded cores originating from the thiophene unit. According to the previous investigation of angular structures in supramolecular liquid crystals, the mesogenic properties

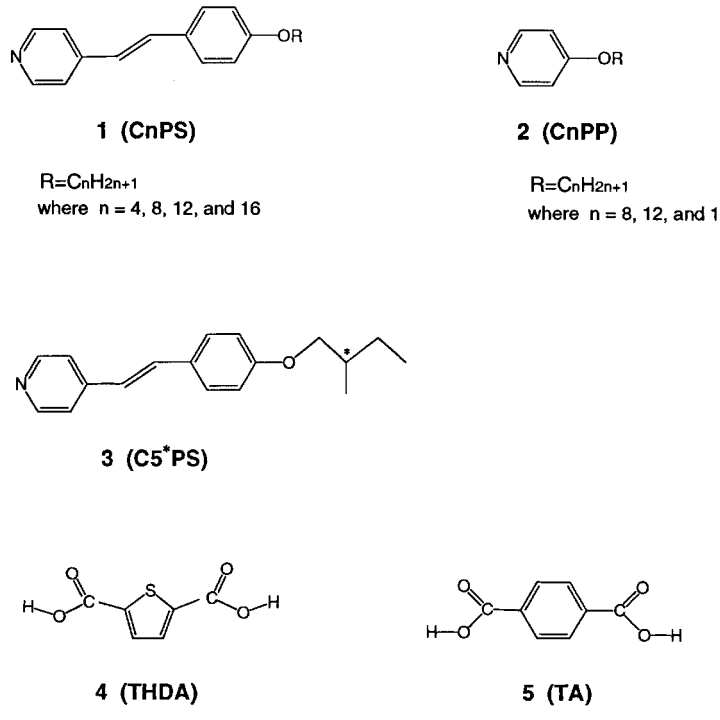

Figure 1. Hydrogen-bonded acceptor and donor moieties.

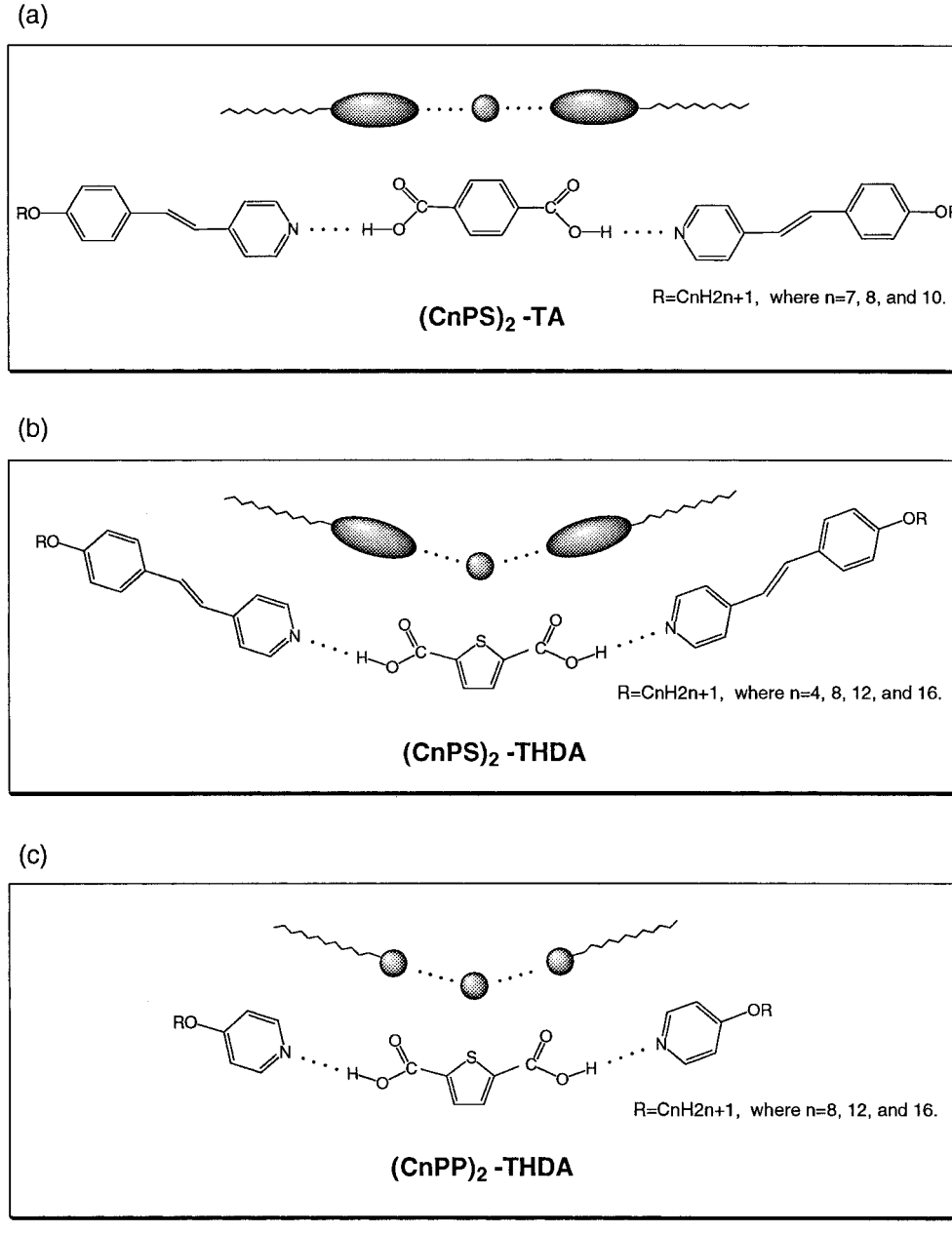

Figure 2. Schematic drawing of hydrogen-bonded complexes (*a*) (C*n*PS)$_2$-TA [16] prepared from a mixture (2:1 molar ratio) of *trans*-4-alkoxystilbazole C*n*PS (**1**) and terephthalic acid TA (**5**); (*b*) (C*n*PS)$_2$-THDA prepared from a mixture (2:1 molar ratio) of C*n*PS (**1**) and thiophenedicarboxylic acid THDA (**4**); (*c*) (C*n*PP)$_2$-THDA prepared from a mixture (2:1 molar ratio) of 4-alkoxypyridine C*n*PP (**2**) and THDA (**4**).

of the double hydrogen-bonded complexes may be affected by the nonlinearity and dipole of the molecular architecture.

The thermal properties of the hydrogen-bonded complexes (C*n*PS)$_2$-THDA, (C5*PS)$_2$-THDA, and (C*n*PP)$_2$-THDA are shown in table 1. In contrast to complexes (C*n*PS)$_2$-TA, complexes (C*n*PS)$_2$-THDA showed lower phase transition (including isotropization) temperatures and distinct mesomorphic properties. For example, upon heating, (C8PS)$_2$-TA melted to an unknown smectic phase at 153°C and decomposed at 250°C [16]; however, (C8PS)$_2$-THDA melted to the smectic A phase at 146·4°C, the nematic phase at 151·4°C, and the isotropic state at 196·7°C. Moreover, THDA (**4**) shows better solubility in the solvent (THF) and better compatibility with C*n*PS (**1**) than does TA (**5**), which has been confirmed by our repeated preparation of these complexes. Overall, the mesomorphic properties of complexes

Table 1. Phase transition temperatures (°C)[a] and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes (C*n*PS)$_2$-THDA, (C5*PS)$_2$-THDA, and (C*n*PP)$_2$-THDA from 2:1 molar ratio of *trans*-4-alkyloxy-4′-stilbazole C*n*PS (**1**)[b], *trans*-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**)[c], or 4-alkyloxypyridine C*n*PP (**2**)[d] complexed with 2,5-thiophenedicarboxylic acid THDA (**4**)[e].

(CnPS)$_2$-THDA										
($n=4$)	Cr	163·1 (67·6)					N	177·2 (69·9) / 222·2 (9·9)		I
($n=8$)[f]	Cr	81·2 (7·3)	Cr′	87·6 (3·7)	Cr″	135·7 (42·3)	SmA	146·9 (1·9)	N	84·8 (4·2) / 151·4 (0·5) / 196·7 (5·8) / 194·5 (4·1)	I
($n=12$)	Cr	66·3 (4·6)			Cr″	128·7 (63·9)	SmA	171·7 (0·3)	N	69·4 (5·0) / 140·3 (64·7) / 175·0 (0·5) / 188·8 (10·0) / 186·0 (11·1)	I
($n=16$)	Cr	40·2 (3·8)	Cr′	68·5 (2·1)	Cr″	117·6 (54·4)	SmC	183·5 (8·3)	N	47·5 (3·9) / 73·9 (2·4) / 134·4 (57·5) / 189·3 (8·4) / 190·4 (4·5) / 186·1 (4·0)	I
(C5*PS)$_2$-THDA										
	Cr	151·4 (2·7)			SmX	158·7 (47·2)			N*	186·0 (73·4) / 184·2 (3·9) / 194·7 (0·6)	I
(CnPP)$_2$-THDA										
($n=8$)	Cr	74·8 (63·9)								84·6 (63·3)	I
($n=12$)	Cr	49·6 (8·1)	SmX	81·1 (89·4)						53·6 (6·3) / 90·0 (90·1)	I
($n=16$)	Cr	55·5 (7·0)	SmX	84·9 (35·5)	SmX′	87·0 (64·5)				59·0 (6·8) / 96·7 (101·7)	I

[a] Phase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling scans (at the heating and cooling rate of 10°C min^{-1}) of differential scanning calorimetry using Perkin Elmer DSC-7; powder X-ray diffraction patterns were obtained from X-ray diffractometer Siemens D-5000 equipped with temperature controller TTK450; abbreviations: Cr, Cr′, Cr″ = crystalline phases, SmX and SmX′ = unidentified smectic phases, N = nematic phase, I = isotropic liquid. The nematic phase was characterized by the schlieren texture coexisting with the homeotropic alignment; the smectic A phase was characterized by the focal-conic fan texture coexisting with the homeotropic alignment; the smectic C phase was characterized by the broken focal-conic fan texture coexisting with the schlieren texture; mesophases were characterized through optical microscopy and confirmed by X-ray diffraction.

[b] The thermal behaviour of *trans*-4-butoxy-4′-stilbazole (C4PS) is: Cr 89·1°C (39·7 J g^{-1}) SmB 93·2°C (31·3 J g^{-1}) I 82·1°C (64·0 J g^{-1}) Cr.

[c] The thermal behaviour of *trans*-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**) is: Cr 99·3°C (87·7 J g^{-1}) I 74·5°C (17·3 J g^{-1}) SmX 69·1°C (51·7 J g^{-1}) Cr.

[d] The thermal properties of 4-alkyloxypyridine C*n*PP (**2**) are: C8PP liquid (at room temp.); C12PP Cr 36·9°C (158·7 J g^{-1}) I (no crystallization upon cooling to room temp.); C16PP Cr 51·5°C (166·1 J g^{-1}) I 30·8°C (167·3 J g^{-1}) Cr.

[e] The melting temperature of 2,5-thiophenedicarboxylic acid THDA (**4**): m.p. > 300°C.

[f] Hydrogen-bonded complex (C8PS)$_2$-TA prepared from 2:1 molar ratio of C8PS and terephthalic acid TA (**5**) has liquid crystalline behaviour as follows (heating): Cr 153°C (69·2 kJ mol^{-1}) Smectic phase 250°C Decomposition [16].

(C*n*PS)$_2$-THDA have the following trend as the alkoxyl chain lengths of C*n*PS (**1**) increase: the nematic phase is favoured at shorter flexible chain lengths, the smectic A phase is favoured at the middle flexible chain lengths ($n=8$ and 12), and the smectic C phase is favoured at the longest flexible chain length ($n=16$). Interestingly, the nematic phase exists in all complexes (C*n*PS)$_2$-THDA, though its temperature range decreases as the alkoxyl chain lengths of C*n*PS increase. The nematic phase is sustained even with very long flexible parts on both sides of these supramolecular liquid crystals, which must be correlated to the central thiophene unit. Therefore, the nonlinearity and dipole of complexes (C*n*PS)$_2$-THDA play important roles in enhancing mesomorphic properties of the supramolecules. As regards the chiral complex (C5*PS)$_2$-THDA, its phase

behaviour matches that of the similar complex $(C4PS)_2$-THDA except that the optically active proton acceptor (*S*)-(-)-*trans*-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**) induces the twisted structure N* by contrast with the nematic phase of $(C4PS)_2$-THDA. The chiral nematic phase N*, i.e. the cholesteric phase, is characterized by the polarizing optical microscope and confirmed by its Grandjean texture coexisting with the focal-conic texture. In addition, by comparison, $(C5*PS)_2$-THDA has a lower isotropization temperature and a narrower range of the mesogenic phase (N*) due to branching of the chiral methyl group to both flexible sides of $(C4PS)_2$-THDA. Thus, the mesogenic structure of the chiral complex may be predicted to possess the twisted form of mesophases in similar supramolecular liquid crystals. Concerning complexes $(CnPP)_2$-THDA with shorter rigid cores obtained by removing two styryl groups from complexes $(CnPS)_2$-THDA, complexes $(CnPP)_2$-THDA do not possess any smectic A, smectic C, or nematic phases, though complexes $(CnPP)_2$-THDA exhibit lower isotropization temperatures than those of complexes $(CnPS)_2$-THDA. This implies that complexes $(CnPP)_2$-THDA containing short supramolecular rigid cores assembled by three single rings through angular H-bonds have poorer mesomorphic properties than complexes $(CnPS)_2$-THDA containing long supramolecular rigid cores.

Table 2 shows the *d*-spacing values of the powder X-ray diffraction (XRD) patterns of complexes $(CnPS)_2$-THDA at $n = 8$, 12, and 16. According to XRD patterns, complexes $(CnPS)_2$-THDA incorporating kinks in the supramolecules may have smectic layer spacings which are approximately the same as the lengths of the supramolecules in bent configurations. The *d*-spacing data (table 2) match molecular lengths calculated from molecular modelling. The lengths of each component calculated by molecular modelling are listed as: C8PS = 20·1 ~ 21·5 Å, C12PS = 24·2 ~ 26·4 Å, C16PS = 28·3 ~ 31·4 Å, and THDA = ~ 8·7 Å; where the latter value is the fully extended molecular length and the former are the molecular projection lengths to the rigid core. The largest *d*-spacings of the SmA and the SmC phases observed in the complexes occur at lower temperatures in the ranges of the smectic A or C phases (see table 2). In summary, the smectic A phase of $(C8PS)_2$-THDA has a *d*-spacing value of 54·2 Å (at 145°C) which is close to the sum (~54 Å) of the fully extended length of each component. However, the smectic A phase of $(C12PS)_2$-THDA has a *d*-spacing 55·4 Å (at 140°C) which is much shorter than the sum (~64 Å) of the fully extended length of each component. Therefore, it suggests that the kinked structure of $(C12PS)_2$-THDA is more pronounced than that of $(C8PS)_2$-THDA. Moreover, the longest complex $(C16PS)_2$-THDA (without

Table 2. X-ray diffraction patterns of hydrogen-bonded complexes $(C8PS)_2$-THDA, $(C12PS)_2$-THDA, and $(C16PS)_2$-THDA at different temperatures.

Complex	Temperature/°C[a]	*d*-spacing/Å[b]
$(C8PS)_2$-THDA	50	23·4 (w), 16·2 (s), 14·0 (s), 3·5 (m)
	90	23·5 (w), 16·4 (s), 14·4 (s), 3·6 (m)
	120	23·4 (s), 19·0 (m), 16·6 (s), 14·6 (s), 12·8 (m), 3·7 (w), 3·6 (w), 3·3 (w)
	140	53·8 (s), 19·0 (s), 12·9 (s), 3·8 (s), 3·7 (s), 3·3 (m)
	145	54·2 (s)[c]
	150	53·7 (s)
	155	53·5 (s)
$(C12PS)_2$-THDA	50	27·3 (w), 24·1 (s), 3·6 (w)
	80	27·6 (w), 24·3 (s), 4·0 (s), 3·7 (w), 3·4 (w)
	120	24·5 (s), 4·0 (w), 3·8 (w), 3·5 (w)
	140	55·4 (s)[c]
$(C16PS)_2$-THDA	50	32·1 (s), 16·0 (w)
	90	32·3 (s), 27·8 (w), 16·2 (w)
	120	27·9 (s), 14·1 (w), 3·9 (w)
	130	50·2 (m)[c], 28·1 (s), 14·1 (w), 4·0 (w)
	140	46·0 (s)
	150	45·3 (s)
	160	45·1 (s)

[a] All temperatures reported were measured on heating scans. Small temperature deviation from DSC data may occur due to the annealing effect in XRD measurements.

[b] s, m, and w are strong, medium, and weak, respectively.

[c] The largest *d*-spacings of the SmA and the SmC phases were observed in these complexes.

the smectic A phase) has a *d*-spacing value of 50·2 Å (at 130°C when the SmC phase just starts to form) which is even shorter than those of the former two complexes, which indicates that both factors of the tilted SmC phase and the kinked structure do exist in $(C16PS)_2$-THDA. Interestingly, no large *d*-spacing values, i.e. no extended supramolecular arrangements, of $(CnPS)_2$-THDA have been observed at lower temperatures, which is distinct from other supramolecular systems [13]. All the complexes form extended supramolecular arrangement in the smectic A or smectic C phases at high temperatures in the $(CnPS)_2$-THDA series. This may be inferred by the easy crystallization of the centre THDA (**4**) in complexes $(CnPS)_2$-THDA at lower temperatures.

In conclusion, new liquid crystalline properties have been introduced by the nonlinear effects of molecular geometry and the dipolar effects of lone-pair electrons in sulphur hetero-atoms. XRD patterns have confirmed their novel molecular architectures. The thiophene-based structures supplying dipoles and bent configurations in the supramolecules can simultaneously reduce the phase transition temperatures of the supramolecules and improve the solubility of the moieties. More importantly, this study illustrates the first thiophene-based molecular architecture in the molecular design of supramolecular liquid crystals. Overall, we have successfully demonstrated novel mesomorphism by bending supramolecules and introducing dipoles in their centres through using the five-membered heterocyclic ring. This thiophene-based nonlinear structure with lone-pair electrons (not contained in the hydrogen bond) providing strong dipoles should be useful in the design of supramolecular liquid crystals.

We are grateful to the Institute of Chemistry, Academia Sinica and the National Science Council of the Republic of China for their support (Grant No. NSC 86-2113-M-001-003).

Appendix

Hydrogen-bonded complexes were prepared by slow evaporation from THF solution containing mixtures of a 1 : 2 molar ratio of the H-bonded donor and acceptor moieties, followed by drying *in vacuo* at 60°C. The proton donor thiophenedicarboxylic acid THDA (**4**) was used as received from Aldrich. The syntheses of proton acceptors are described as follows:

*Syntheses of 4-alkoxy-4'-stilbazoles CnPS (**1**) and 4-(2-methylbutoxy)-4'-stilbazole C5*PS (**3**)*

Hydrogen-bonded acceptor moieties *trans*-4-alkoxy-4′-stilbazoles C*n*PS (**1**) ($n = 4$, 8, 12, and 16; where n is the number of carbons in the alkoxy chain) and *trans*-4-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**) were identified as the required products and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy. Elementary analytical results for C, H and N were also satisfactory. The synthesis of optically active (*S*)-(-)-*trans*-(2-methylbutoxy)-4′-stilbazole C5*PS (**3**) will be reported elsewhere. Synthetic routes for *trans*-4-alkoxy-4′-stilbazoles C*n*PS (**1**) were followed as described in the literature [30, 31]. The characterization data of recently synthesized C4PS are shown below, other complexes were described in our previous publication [31].

Trans-4-butoxy-4'-stilbazole (C4PS)

^{1}H NMR δ ($CDCl_3$) 0·99 (t, 3H, CH_3), 1·47–1·54 (m, 2H, CH_2), 1·76–1·81 (m, 2H, OCH_2CH_2), 4·00 (t, 2H, OCH_2), 6·85 (s, 1H, CH=), 6·91 (d, 2H, $J = 7{\cdot}34$ Hz, 2 × Phenyl–H), 7·27 (d, 1H, $J = 16{\cdot}21$ Hz, CH=), 7·35 (d, 2H, $J = 5{\cdot}52$ Hz, 2 × Pyridyl–H), 7·47 (d, 2H, $J = 8{\cdot}69$ Hz, 2 × Phenyl–H), 8·56 (s, 2H, 2 × Pyridyl–H). ^{13}C NMR δ ($CDCl_3$) 13·81, 19·21, 31·25, 67·79, 114·82, 120·59, 123·55, 128·34, 128·67, 132·78, 145·02, 150·07, 159·78. Elemental analysis for $C_{17}H_{19}NO$: calculated C 80·59, H 7·56, N 5·52; found C 80·51, H 7·67, N 5·53%.

*Syntheses of 4-alkoxypyridines CnPP (**2**)*

Synthetic routes for 4-alkoxypyridines C*n*PP (**2**) were followed as described in the literature [32]. 80% of sodium hydride (48·0 mmol) was weighed and stirred with 25 ml of dried hexane in a reaction flask. 10 ml of dried dimethylsulphoxide was added after removing the hexane. The mixture was allowed to stir for 1·5 h before the appropriate alcohol (19·2 mmol) was added dropwise. (If the alcohol was a solid, a concentrated solution in dimethylsulphoxide was employed.) After the alcohol had been added, 4-chloropyridine (28·8 mmol) was added and the solution allowed to stir overnight at room temperature. [4-Chloropyridine was prepared by neutralization of hydrochloride salt (30 g; 0·20 mol) dissolved in about 200 ml of water, and then cooled in an ice bath during dropwise addition of 120 ml of 10% sodium hydroxide till dark brown. The solution was then extracted with pentane and the combined extracts were dried over anhydrous sodium sulphate. After filtration and evaporation of the solvent, the product was distilled at room temperature under vacuum to give the desired 4-chloropyridine in 50% yield.] When the reaction had finished, 50 ml of water was added and the solution extracted with ethyl acetate (50 × 2 ml). The combined extracts were dried over anhydrous sodium sulphate, evaporated at reduced pressure and purified by chromatography on silica to give the desired 4-aloxypyridines in 10–53% yield. 4-Alkoxypyridines C*n*PP (**2**) were identified as the required products and judged to be pure by ^{1}H and ^{13}C NMR spectroscopy.

Elementary analytical results for C, H, and N were also satisfactory. Their data are given below.

4-Octyloxypyridine (C8PP)

^{1}H NMR δ ($CDCl_3$): 0·89 (t, 3H, $J = 6{\cdot}76$ Hz, CH_3), 1·29–1·45 (m, 10H, $5 \times CH_2$), 1·72–1·81 (m, 2H, $J =$ 6·49 Hz, OCH_2CH_2), 3·94 (t, 2H, $J = 6{\cdot}53$ Hz, OCH_2), 6·76 (d, 2H, $J = 6{\cdot}08$ Hz, $2 \times$ Pyridyl–H), 8·38 (d, 2H, $J = 6{\cdot}04$ Hz, $2 \times$ Pyridyl–H). ^{13}C NMR δ ($CDCl_3$): 13·48, 22·06, 25·34, 28·29, 28·63, 28·71, 31·21, 67·19, 109·60, 150·34, 164·41. Elemental analysis for $C_{13}H_{21}NO$: calculated C 75·32, H 10·21, N 6·76; found C 75·20, H 10·36, N 6·72%.

4-Dodecyloxypyridine (C12PP)

^{1}H NMR δ ($CDCl_3$): 0·88 (t, 3H, $J = 6{\cdot}54$ Hz, CH_3), 1·27–1·42 (m, 18H, $9 \times CH_2$), 1·71–1·80 (m, 2H, $J =$ 6·37 Hz, OCH_2CH_2), 3·92 (t, 2H, $J = 6{\cdot}53$ Hz, OCH_2), 6·74 (d, 2H, $J = 4{\cdot}95$ Hz, $2 \times$ Pyridyl–H), 8·37 (d, 2H, $J = 5{\cdot}23$ Hz, $2 \times$ Pyridyl–H). ^{13}C NMR δ ($CDCl_3$): 13·60, 22·20, 25·44, 28·40, 28·88, 29·12, 29·18, 31·44, 67·26, 109·66, 150·43, 164·48. Elemental analysis for $C_{17}H_{29}NO$: calculated C 77·51, H 11·10, N 5·32; found C 77·77, H 11·17, N 5·21%.

4-Hexadecyloxypyridine (C16PP)

^{1}H NMR δ ($CDCl_3$): 0·88 (t, 3H, $J = 6{\cdot}86$ Hz, CH_3), 1·26–1·45 (m, 26H, $13 \times CH_2$), 1·74–1·83 (m, 2H, $J =$ 6·54 Hz, OCH_2CH_2), 3·98 (t, 2H, $J = 6{\cdot}50$ Hz, OCH_2), 6·78 (d, 2H, $J = 5{\cdot}88$ Hz, $2 \times$ Pyridyl–H), 8·40 (d, 2H, $J = 5{\cdot}38$ Hz, $2 \times$ Pyridyl–H). ^{13}C NMR δ ($CDCl_3$): 14·02, 22·59, 25·82, 28·78, 29·24, 29·27, 29·48, 29·59, 31·83, 67·75, 110·13, 150·88, 164·95. Elemental analysis for $C_{21}H_{37}NO$: calculated C 78·94, H 11·67, N 4·38; found C 78·78, H 11·74, N 4·20%.

References

[1] Pei, Q., and Yang, Y., 1995, *Adv. Mater.*, **7,** 559; Chen, X. L., and Jenekhe, A., 1996, *Macromolecules*, **29,** 6189; Noda, T., Imae, I., Noma, N., and Shirota, Y., 1997, *Adv. Mater.*, **9,** 239.

[2] Abe, J., and Shirai, Y., 1996, *J. Am. chem. Soc.*, **118,** 4705; Varanasi, P. R., Jen, A. K.-Y., Chandrasekhar, J., Namboothiri, I. N. N., and Rathna, A., 1996, *J. Am. chem. Soc.*, **118,** 12443; Wong, M. S., Meier, U., Pan, F., Gramlich, V., Bosshard, C., and Gunter, P., 1996, *Adv. Mater.*, **8,** 416.

[3] Chou, S. S. P., Sun, D. J., Lin, H. C., and Yang, P. K., 1996, *Chem. Commun.*, 1045; Chou, S. S. P., Sun, D. J., Huang, J. Y., Yang, P. K., and Lin, H. C., 1996, *Tetrahedron Lett.*, **37,** 7279.

[4] Lai, L. L., Wang, C. H., Hsieh, W. P., and Lin, H. C., 1996, *Mol. Cryst. liq. Cryst.*, **287,** 177; Lin, H. C., Lai, L. L., Hsieh, W. P., and Huang, W. Y., 1997, *Liq. Cryst.*, **22,** 661.

[5] Lehn, J. M., 1988, *Angew. Chem. int. Ed. Engl.*, **27,** 89.

[6] Desiraju, G. R., 1995, *Angew. Chem. int. Ed. Engl.*, **34,** 2311.

[7] Kato, T., and Fréchet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[8] Kato, T., Fujishima, A., and Fréchet, J. M. J., 1990, *Chem. Lett.*, 919.

[9] Kato, T., Wilson, P. G., Fujishima, A., and Fréchet, J. M. J., 1990, *Chem. Lett.*, 2003.

[10] Kato, T., Fréchet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Jin, C., and Kaneuchi, F. M. J., 1993, *Chem. Mater.*, **5,** 1094.

[11] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. int. Ed. Engl.*, **34,** 1696.

[12] Wallace, M. J., and Imrie, C. T., 1997, *J. mater. Chem.*, **7,** 1163.

[13] Lin, H. C., and Lin, Y. S., 1998, *Liq. Cryst.*, **24,** 315.

[14] Willis, K., Price, D. J., Adams, H., Ungar, G., and Bruce, D. W., 1995, *J. mater. Chem.*, **5,** 2195.

[15] Price, D. J., Willis, K., Richardson, T., Ungar, G., and Bruce, D. W., 1997, *J. mater. Chem.*, **7,** 883.

[16] Kato, T., Adachi, H., Fujishima, A., and Fréchet, J. M. J., 1992, *Chem. Lett.*, 265.

[17] Willis, K., Luckhurst, J. E., Price, D. J., Fréchet, J. M. J., Kihara, H., Kato, T., Ungar, G., and Bruce, D. W., 1996, *Liq. Cryst.*, **21,** 585.

[18] Brettle, R., Dunmur, D. A., Marson, C. M., Pinol, M., and Toriyama, K., 1993, *Liq. Cryst.*, **13,** 515.

[19] Butcher, J. L., Byron, D. J., Matharu, A. S., and Wilson, R. C., 1995, *Liq. Cryst.*, **19,** 387.

[20] Seed, A. J., Toyne, K. J., and Goodby, J. W., 1995, *J. mater. Chem.*, **5,** 653.

[21] Byron, D. J., Komitov, L., Matharu, A. S., McSherry, I., and Wilson, R. C., 1996, *J. mater. Chem.*, **6,** 1871.

[22] Hoppe, F. D., and Koßmehl, G., 1996, *Liq. Cryst.*, **21,** 255.

[23] Iglesias, R., Serrano, J. L., and Sierra, T., 1997, *Liq. Cryst.*, **22,** 37.

[24] Cai, R., and Samulski, E. T., 1991, *Liq. Cryst.*, **9,** 617.

[25] Gallardo, H., and Favarin, I., 1993, *Liq. Cryst.*, **13,** 115.

[26] Koßmehl, G., and Hoppe, F. D., 1993, *Liq. Cryst.*, **15,** 383.

[27] Koßmehl, G., and Hoppe, F. D., 1994, *Mol. Cryst. liq. Cryst.*, **257,** 169.

[28] Butcher, J. L., Byron, D. J., Matharu, A. S., and Wilson, R. C., 1995, *Liq. Cryst.*, **19,** 387.

[29] Bunning, J. D., and Butcher, J. L., 1996, *Liq. Cryst.*, **20,** 103.

[30] Bruce, D. W., Dunmur, D. A., Lalinde, E., Maitlis, P. M., and Styring, P., 1988, *Liq. Cryst.*, **3,** 385.

[31] Lin, H. C., Lai, L. L., Lin, Y. S., Tsai, C. T., and Chen, R. C., *Mol. Cryst. liq. Cryst.* (in press).

[32] Schmid, G. H., and Wolkoff, A. W., 1972, *Can. J. Chem.*, **50,** 1181.