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Preliminary communication

The effects of bending sites on unconventionally shaped hydrogen-bonded liquid crystals

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Angular mesogenic structures of hydrogen-bonded supramolecules have been constructed from a 1:1 molar ratio of 3(or 4)-decyloxybenzoic acid, MA (or PA), mixing either with *trans*-4-alkoxy-3'(or 4')-stilbazoles, C_nM (or C_nP), or with their analogous *N*-oxides (C_nMO and C_nPO) to form the hydrogen-bonded (H-bonded) complexes C_nPPA , C_nPMA , C_nMPA , C_nPOPA , C_nPOMA and C_nMOPA . By controlling the relative bending position of the H-bonded complexes, the variety of supramolecules offer new molecular structures of different linearities. By means of these bending effects we are able to tune the shape of the molecular architecture and thus to modify molecular packing as well as mesogenic properties. New liquid crystalline properties are introduced by the nonlinear effects of molecular geometry, and powder X-ray diffraction (XRD) patterns have confirmed their novel molecular architectures.

Molecular recognition, making use of moieties with different specific selectivities at the molecular level, has been studied in recent years [1–4]. Hydrogen bonding is one of the most important non-covalent forces encountered in the fields of chemistry and biology, leading to molecular aggregation and the formation of supramolecules. Recently the hydrogen bonds of unlike species have been utilized to generate self-assembled phases, i.e. mesogenic phases, which are different from those of their original moieties [5–9].

Conventionally, molecular structures consisting of rigid cores with flexible attachments are favoured to exhibit mesogenic properties in a linear form. Four liquid crystalline materials are derived from 1,2- or 1,3-disubstituted benzenes whose molecules are kinked at the aromatic rings [10, 11]. The limited tendency of angular molecules to form mesogenic phases is also noticed in the nonparallel configuration caused by an angular bridging group, such as $-O-$, $-S-$, $-NH-$ and $-CH_2-$ [11]. Hence, the presence of linearity of the molecular architecture is preferred in traditional thermotropic liquid crystals. Additionally, several liquid crystalline structures containing rigid cores of nonlinear configurations, such as five-membered heterocyclic rings (e.g. thiophenes, pyrazoles and isoxazoles) [12–17], are generally thought less conducive to liquid crystalline

phase formation than six-membered rings, owing to the bond angles of the five-membered rings. Nevertheless, nonlinear systems generally possess lower melting temperatures than those of their analogous linear counterparts due to the reduced packing efficiency of the molecules. Hence, it has been found that some five-membered heterocyclic rings [12–17] promote the stability of mesogenic phases, as compared with 1,4-disubstituted phenyl analogues. Moreover, lateral dipoles within the heterocyclic structures can enhance negative dielectric anisotropy, which may avoid the disadvantage of system broadening and increase of viscosity caused by lateral polar substituents [18, 19].

Recently, a number of publications have reported 1,2-disubstituted phenyl derivatives with obtuse- and acute-angled configurations, such as U- or V-shaped dimeric structures; these demonstrate unique mesomorphic properties with the bending site in the centre of the dimeric liquid crystalline structures [20–22]. Disubstitutions in the naphthalene ring also offer molecular shapes of different linearities which significantly influence both liquid crystalline behaviour and ferroelectric properties [23]. The hydrogen-bonded complexes reported previously also show stable mesophases with linear structures similar to traditional liquid crystals [5–9].

Only very limited information concerning the effects of nonlinear H-bonded structures on mesomorphism could

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be obtained from the literature [24–26]. Willis *et al.* [24] showed that the hydrogen-bonded complex formed by mixing 4-cyanophenol and *trans*-4-alkoxystilbazole appeared to be kinked, and the bend was introduced by the nonlinear mesogen. Using the more linear complex structure of 3-cyanophenol instead of 4-cyanophenol, the mesomorphic properties were more stable. However, the thermally annealed complexes between phthalic acid and decyloxystilbazole containing double hydrogen bonds and two long flexible tails showed different behaviour [26] from the previous publication [25]. Thus, the effects of nonlinear structures on the mesomorphism of supramolecules are still equivocal. Here, we would like to report the first systematic investigation of angular supramolecules containing various bending sites.

Our recent work has shown that different kinked structures with various bending sites provided by angular H-bonded complexes could reveal novel mesomorphic behaviour. In order to understand the effects of nonlinear geometry on H-bonded complexes, the bend structures are derived either from the bend between the rigid core and the flexible part or from the nonlinear rigid core containing the angular H-bond (figure 1). Supramolecules (*C_nPPA*, *C_nPMA*, *C_nMPA*, *C_nPOPA*, *C_nPOMA* and *C_nMOPA*) with possible arrangements of various nonlinearities (bending positions of 2 and 3 in figure 1), assuming a linear hydrogen bond between N...H–O (or O...H–O), were prepared in this study from 1:1 molar ratios of H-bonded acceptor [27,28] and donor moieties (figure 2). Accordingly, alteration of

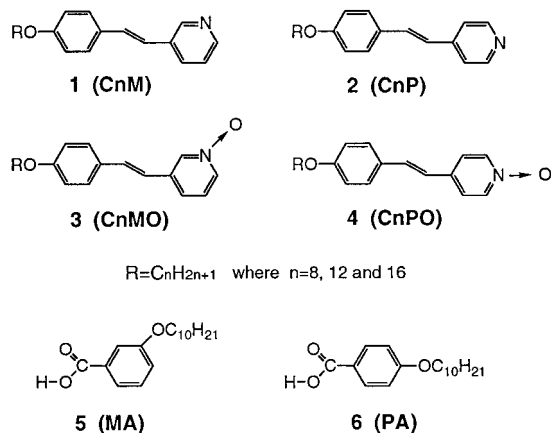


Figure 2. Hydrogen-bonded acceptor and donor moieties.

the bending sites of the supramolecules has been used systematically for the first time to analyse the mesogenic behaviour of angular H-bonded complexes, enabling us to visualize the role of hydrogen bonds in the bend structures.

Mesogenic properties of the hydrogen-bonded acceptors *C_nM*, *C_nP*, *C_nMO* and *C_nPO* ($n = 8, 12$, and 16) were reported in our previous publication [28]. *C_nM* and *C_nP* ($n = 8, 12$, and 16) show narrow ranges of smectic B and E phases; *C_nMO* and *C_nPO* ($n = 8, 12$, and 16) show a monotropic or an enantiotropic smectic A phase. Thermal properties of the hydrogen-bonded donors MA (3-decyloxybenzoic acid) and PA (4-decyloxybenzoic acid) are as follows. MA heating:

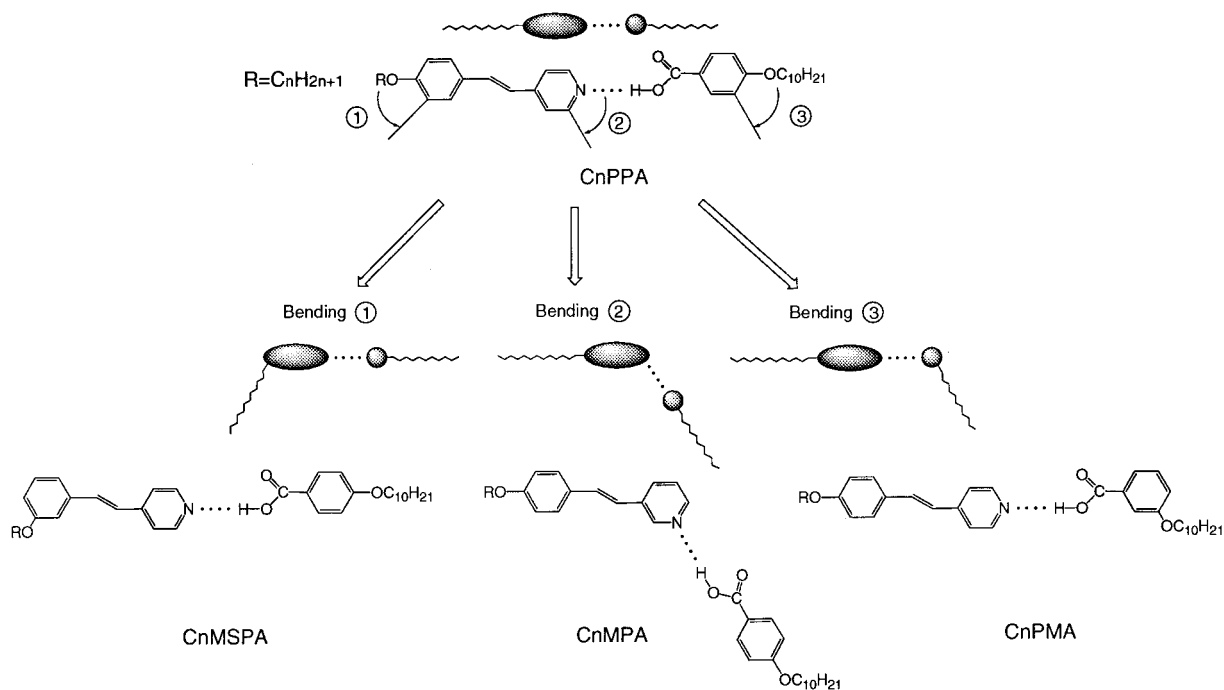


Figure 1. Hydrogen-bonded complexes with possible structures of various nonlinearities through bending at different sites.

Cr 78.6°C (21.9 J g⁻¹) Sx 82.3°C (132.7 J g⁻¹) I; MA cooling: I 72.4°C (154.0 J g⁻¹) Cr: PA heating: Cr 85.1°C (58.9 J g⁻¹) Sx 96.0°C (30.3 J g⁻¹) SmC 123.7°C (4.5 J g⁻¹) N 142.4°C (7.7 J g⁻¹) I; PA cooling: I 139.6°C (7.2 J g⁻¹) N 120.5°C (4.3 J g⁻¹) SmC 90.2°C (31.1 J g⁻¹) Sx 69.4°C (21.5 J g⁻¹) Cr. Tables 1 and 2 show the thermal properties of these H-bonded complexes (C_nPPA, C_nPMA, C_nMPA, C_nPOPA, C_nPOMA and C_nMOPA) which are different from those of their constituent moieties. For instance, the SmA and SmF phases of C_nPPA, the SmA and SmC phases of C_nPMA, and the SmA phase of C16MPA are all different from those of their constituents.

Figures 3 and 4 illustrate the phase transition temperatures and possible molecular structures of the supra-molecular complexes. In general, both the C_nPPA and C_nPOPA systems have higher phase transition temperatures than their respective comparable systems. In addition, some kinked structures exhibit mesogenic phases that are not observed in the linear structures. For example, C_nPMA possesses an enantiotropic SmA phase and C16MPA possesses a monotropic SmA phase, whereas the linear structures of C12PPA and C16PPA do not possess any SmA phases. Another interesting phenomenon is that the enantiotropic SmC phase is introduced in C_nPMA (kinked between the core and

Table 1. Phase transition temperatures (°C)^a and corresponding enthalpies (J g⁻¹), in parentheses, of hydrogen-bonded complexes from a 1:1 molar ratio of 3(or 4)-decyloxybenzoic acid and *trans*-4-alkoxy-3'(or 4')-stilbazole (C_nPPA, C_nPMA and C_nMPA).

PPA (n = 8)	Cr	70.9 (25.0)	SmX	75.9 (59.5)	SmF	116.4 (4.2)	SmC	141.4 (0.3)	SmA	156.8 (23.8)	I
			51.6 (8.5)		57.1 (58.7)		113.2 (3.0)		138.5 (0.3)		153.0 (23.1)
(n = 12)	Cr	75.4 (63.3)	SmX	77.5 (12.3)	SmF	111.2 (5.2)	SmC		152.0 (31.1)		I
			40.7 (33.0)		45.2 (28.4)		108.3 (4.1)		148.6 (28.1)		
(n = 16)	Cr		77.7 (65.6)			125.2 (10.7)	SmC		151.2 (29.1)		I
			64.5 (62.4)			121.8 (9.9)			147.9 (26.9)		
PMA (n = 8)	Cr		56.4 (84.1)				SmC	59.2 (0.3)	SmA	79.5 (7.3)	I
								53.9 (0.1)		76.6 (7.3)	
(n = 12)	Cr		64.2 (91.3)				SmC	73.6 (0.2)	SmA	83.4 (7.0)	I
								70.9 (0.1)		80.4 (6.3)	
(n = 16)	Cr		70.7 (64.5)				SmC	79.2 (0.3)	SmA	85.6 (5.1)	I
								76.1 (0.1)		82.2 (4.2)	
MPA (n = 8)	Cr	57.5 (34.3)	Cr'				64.0 (55.6)				I
			37.2 (3.8)				47.2 (71.9)				
(n = 12)	Cr					70.2 (103.5)					I
						56.0 (101.7)					
(n = 16)	Cr	71.2 (40.5)	SmX			75.6 (79.9)					I
						57.4 (91.9)		SmA		66.5 (6.0)	

^aPhase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling scans (at a 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 an X-ray diffractometer Siemens D-5000 equipped with a temperature controller TTK450. Abbreviations: Cr and Cr' = crystalline phases, SmX = unidentified smectic phase, I = isotropic liquid. The orthogonal smectic A phase was characterized by a focal-conic fan texture coexisting with homeotropic alignment; the tilted smectic C phase was characterized by a broken focal-conic fan texture coexisting with schlieren texture; the tilted smectic F phase was characterized by the paramorphic schlieren-mosaic texture formed on cooling the schlieren texture of the smectic C phase; mesophases were characterized by optical microscopy and were also confirmed by XRD.

Table 2. Phase transition temperatures ($^{\circ}\text{C}$) and corresponding enthalpies (J g^{-1}), in parentheses, of hydrogen-bonded complexes from a 1:1 molar ratio of 3(or 4)-decyloxybenzoic acid and *N*-oxide of 4-alkyloxy-3'(or 4')-stilbazole (C_nPOPA , C_nPOMA and C_nMOPA).

POPA ($n = 8$)	Cr	104.1 (54.2)			SmA	123.7 (10.7)	I		
		92.2 (54.0)				121.2 (10.6)			
		95.7 (90.2)	98.5 (4.4)	108.0 ^a	130.8 (9.7)				
(n = 12)	Cr	76.0 (42.1)	SmX	89.1 (45.0)	SmC	104.0 ^a	SmA	128.4 (9.6)	I
		80.2 (7.7)		94.8 (77.6)		109.8 (0.4)		122.6 (7.8)	
(n = 16)	Cr	78.3 (37.7)	SmX	81.1 (39.9)	SmC	107.0 (0.6)	SmA	121.0 (7.2)	I
POMA (n = 8)	Cr	46.2 ^b	SmX	52.4 ^b			SmA	59.1 (7.7)	I
								57.5 (5.9)	
								73.1 (5.1)	
(n = 12)	Cr			61.3 (61.1)			SmA	72.4 (5.7)	I
								76.2 (2.8)	
								67.0 (2.9)	
(n = 16)	Cr	61.1 (22.7)	SmX	69.2 (57.4)			SmA	76.2 (2.8)	I
								67.0 (2.9)	
MOPA (n = 8)	Cr	47.8 (1.4)	Cr'	83.0 (2.5)	Cr''	110.1 (88.3)	SmA	97.1 (18.2)	I
		41.3 (1.2)		76.7 (67.0)		SmC	92.0 ^a		
(n = 12)	Cr			111.4 (87.2)			SmA	103.8 (18.8)	I
								101.8 ^a	
(n = 16)	Cr			103.6 (70.4)			SmA	101.0 (17.9)	I
								100.0 ^a	

^aThe enthalpy was too small to be detected by DSC and the phase transition temperature was assigned by polarizing optical microscope.

^bThe peaks are overlapped and their total enthalpy is 14.9 J g^{-1} .

Abbreviations: Cr, Cr' and Cr'' = crystalline phases, SmX = unidentified smectic phase.

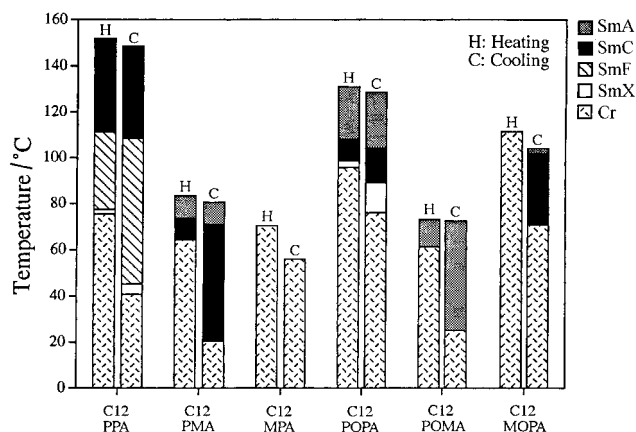


Figure 3. Phase transition temperatures of hydrogen-bonded complexes (C12) PPA, PMA, MPA, POPA, POMA and MOPA.

the flexible part) neither of whose constituents C_nP and MA have a SmC phase; however, the SmC phase is not observed in C_nMPA (kinked in the rigid core bearing the H-bond) containing the constituent PA which does possess a SmC phase. Furthermore, the C_nMPA system exhibits the worst mesomorphic behaviour at short alkoxy lengths (at $n \leq 12$) except that C16MPA shows a monotropic SmA phase. This may suggest that the SmC phase is more favoured in a supramolecular architecture with the kink in the flexible part than with the kink in the rigid core, though some kinked structures in the core, such as five-membered heterocyclic rings, as well as in aliphatic linkage favour the occurrence of a SmC phase [17, 29–31]. The kink in the angular hydrogen-bonded mesogen of C_nMPA (see figure 4) may explain the lower stability of the mesophases; nevertheless, this kink can be compensated by the longer alkoxy chain length in C16MPA . In the *N*-oxide series,

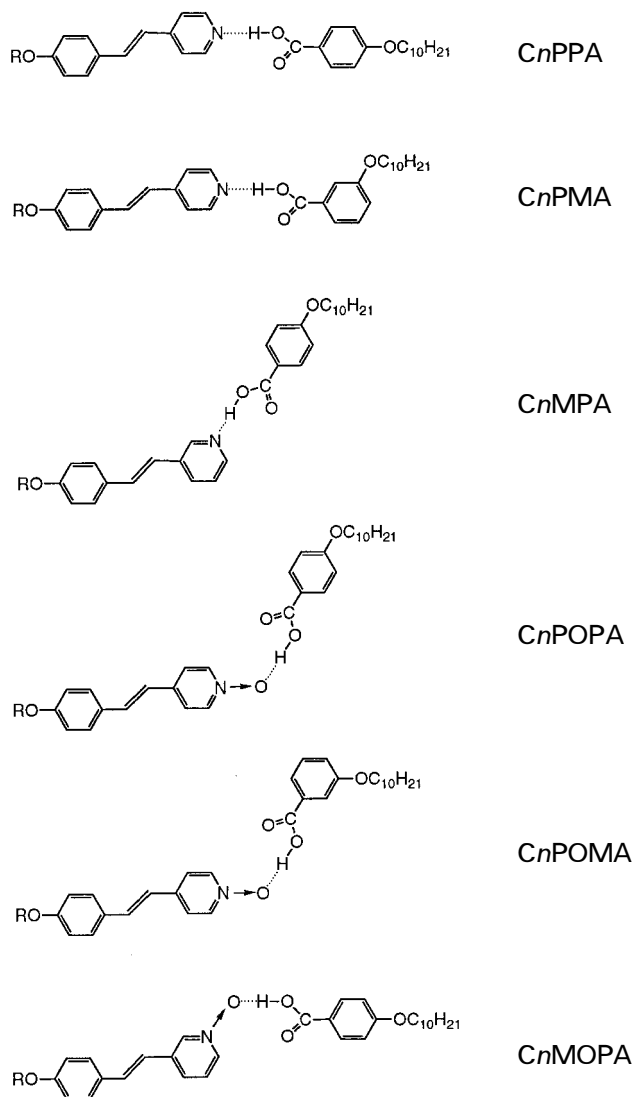


Figure 4. Possible schematic structures of hydrogen-bonded complexes with various degrees of nonlinearities.

the C_nMOPA systems exhibits a monotropic SmC phase and the C_nPOMA system (kinked in the rigid core bearing the H-bond) does not exhibit the SmC phase. Moreover, C₈POPA (kinked in the rigid core bearing the H-bond) does not show a SmC phase, in contrast to C₈MOPA. In addition, only the C_nMOPA system shows monotropic SmA and SmC phases (along with C₁₆MPA exhibiting a monotropic SmA phase) during the cooling process, so the monotropic phenomena are favoured in these special supramolecular structures.

Furthermore, IR and powder X-ray diffraction (XRD) measurements reveal the H-bonds that have formed in the H-bonded complexes. XRD measurements also prove that some bend structures are less kinked than originally thought. If the SmA phase is assumed to have a more linear structure than any other mesophases (especially,

the largest *d*-spacings of the SmA phase were observed at the lowest temperatures of the SmA phase in each heating or cooling cycle), it would be considered useful to relate the kinked structures to the bend in the hydrogen-bonded core or to the bend between the core and the terminal chain end. Table 3 shows the largest *d*-spacing values of the SmA phase which were obtained from XRD measurements. Since the largest *d*-spacing of the SmA phase (molecule orthogonal to the layer) is correlated to the length of the supramolecule, the degree of bend can be estimated from the XRD data. The *d*-spacing data (table 3) match molecular lengths calculated from molecular modelling (see figure 4). The lengths of each component calculated by molecular modelling are listed as: C₈M (or C₈MO) = 20.1 ~ 21.5 Å, C₁₂M (or C₁₂MO) = 24.2 ~ 26.4 Å, C₁₆M (or C₁₆MO) = 28.3 ~ 31.4 Å, MA = 17.4 ~ 20.5 Å, and PA = 19.1 ~ 20.6 Å; where the latter value is the fully extended molecular length and the former value is the molecular projection length to the rigid core. The molecular shapes of figure 4 were confirmed by molecular modelling (quantum mechanical calculation) and these detailed results will be published later.

From table 3, it is found that the most linear structure of these supramolecular systems is C_nPPA, since C₈PPA has the longest *d*-spacing for all systems at alkoxy length *n* = 8. All the other systems have similar molecular lengths in the SmA phase, all shorter than C_nPPA. These results indicate that all the systems are kinked in shape to a similar extent, except for C_nPPA. The explanation for the similar lengths of these different supramolecules may be the higher flexibility of the H-bond compared with the covalent bond. Another peculiarity observed in C_nPOMA is that *d*-spacings of repeated heating cycles are smaller than those of repeated cooling cycles, and the longer the flexible lengths the larger the differences in *d*-spacings. Thus, the degree of bend in C_nPOMA is decreased by cooling from the isotropic state, and the *d*-spacings of the cooling cycle are closer to those of the other systems. This strongly suggests that the nonlinearity of the kinked structure in C_nPOMA is dependent on its thermal history and flexible length. This is possibly because the double kinks (one kink between the core and the flexible part, the other in the rigid core bearing the H-bond) in the molecular structure of C_nPOMA (see figure 4) can be organized into a more linear form upon cooling from the isotropic state with its higher flexibility and mobility; whereas, upon heating from the highly ordered phase, the doubled kinked structure is more difficult to rearrange into the longest length form. Also, the longer flexible length may enhance this phenomenon through hydrophobic interactions among alkoxy chains. According to table 3, this implies that both C₁₆POMA and

Table 3. The largest d -spacing of the smectic A phase in the hydrogen-bonded complexes C_n PPA, C_n PMA, C_n MPA, C_n POPA, C_n POMA and C_n MOPA.

Complex	d -Spacing Å ^a		Complex	d -Spacing Å	
	Heating	Cooling		Heating	Cooling
PPA			POPA		
($n = 8$)	43·16 (145°C)	42·39 (135°C)	($n = 8$)	38·07 (105°C)	38·41 (100°C)
($n = 12$) ^b			($n = 12$)	40·38 (115°C)	40·61 (110°C)
($n = 16$) ^b			($n = 16$)	43·14 (105°C)	44·17 (105°C)
PMA			POMA		
($n = 8$)	38·42 (65°C)	38·65 (60°C)	($n = 8$)	35·49 (55°C)	36·39 (40°C)
($n = 12$)	39·26 (75°C)	39·09 (74°C)	($n = 12$)	38·26 (63°C)	41·60 (35°C)
($n = 16$)	43·81 (80°C)	43·12 (78°C)	($n = 16$)	39·23 (65°C)	45·53 (45°C)
MPA			MOPA		
($n = 8$) ^b			($n = 8$) ^c		38·26 (95°C)
($n = 12$) ^b			($n = 12$) ^c		39·42 (104°C)
($n = 16$) ^c		43·12 (72°C)	($n = 16$) ^c		44·34 (100°C)

^aTemperatures in parentheses are the temperatures at which the largest d -spacings were measured (the largest d -spacings of the SmA phase were observed at the lowest temperatures of the SmA phase in each heating or cooling cycle). Small temperature deviation from DSC data may occur due to the annealing effect in XRD measurements.

^bNo smectic A phase observed.

^cMonotropic smectic A phase observed.

C12POMA can be regarded as the most linear form (the longest length by X-ray) compared with their analogous systems, while both the C16PMA and C16MPA systems are more kinked than C16POMA. This agrees with the possible schematic structures shown in figure 4. C_n POPA possesses similar d -spacings to C_n MOPA (table 3), so C_n POPA is possibly not as kinked as expected from figure 4. From these results it may be inferred that the molecular bend structures are similar in most of the angular systems, and that the hydrogen bonds of the various molecular shapes in figure 4 must be more flexible than expected. Overall, the d -spacings in table 3 suggest that C_n PPA has the most linear structure of these supramolecular systems. Consequently, further XRD measurements to confirm their novel molecular arrangements, together with detailed X-ray data, will be reported elsewhere.

In general, compared with the melting temperatures of these hydrogen-bonded complexes, fewer experiments are needed to obtain the clearing temperatures of the blends. Therefore, the clearing temperatures (T_c) of mixtures can be more reliably predicted since they tend to be linear functions [10] of the T_{ci} s of their constituent components.

$$T_c = \Sigma(T_{ci} \times X_i) \quad (1)$$

where T_{ci} is the clearing temperature of the component i and X_i is the mole ratio of the component i in the mixture. Significantly, this relation holds better when compounds of similar polarities are mixed, otherwise the larger difference in their polarities causes a larger

negative deviation from ideal behaviour. Since the clearing temperatures (T_{ci}) of all constituent components in our study are very distinct, the experimental T_c (T_2) values of different shaped complexes with hydrogen-bonded interactions cannot be strictly compared without considering the T_{ci} values of their individual components. In order to analyse the effect of hydrogen-bonded complex formation, the deviation temperatures (ΔT) of all complexes—i.e. the experimental T_c (T_2) values with hydrogen-bonded interactions minus the theoretical T_c (T_1) values without molecular interactions—must be compared. Table 4 shows theoretical T_c (T_1) values obtained from equation (1), the experimental T_c (T_2) values and the deviation values (ΔT) for all complexes. From the deviation temperatures (ΔT) of these complexes, the effect of the bend in hydrogen-bonded structures can be justifiably examined. According to table 4 and figure 4, we can conclude that the deviation temperature (ΔT) has been exclusively enhanced in PPA (positive enhancement $\Delta T = 36·4^\circ\text{C}$) for its most linear structure after complex formation through hydrogen-bonding. The other systems have negative effects on the clearing temperatures due to the different degrees of nonlinearities in the kinked supramolecular structures.

Another interesting result is that the N -oxide supramolecules show lower clearing (isotropization) temperatures (T_2) and lower ΔT values than their non-oxide analogues, except MOPA. For example, PPA ($T_2 = 152·0^\circ\text{C}$; $\Delta T = +36·4^\circ\text{C}$) > POPA ($T_2 = 130·8^\circ\text{C}$; $\Delta T = -9·6^\circ\text{C}$) and PMA ($T_2 = 83·4^\circ\text{C}$; $\Delta T = -2·2^\circ\text{C}$) > POMA ($T_2 = 73·1^\circ\text{C}$; $\Delta T = -37·2^\circ\text{C}$). In these cases, the

Table 4. Theoretical clearing temperatures (T_1), experimental clearing temperatures (T_2), and deviation temperatures $\Delta T(T_2-T_1)$ of C12PPA, C12PMA, C12MPA, C12POPA, C12POMA and C12MOPA.

Complex	$T_1/^\circ\text{C}$ (Theoretical T_c) ^a	$T_2/^\circ\text{C}$ (Experimental T_c) ^b	$\Delta T/^\circ\text{C}$ (T_2-T_1) ^c
C12PPA	115.6	152.0	+36.4
C12PMA	85.6	83.4	-2.2
C12MPA	113.2	70.2	-43.0
C12POPA	140.4	130.8	-9.6
C12POMA	110.3	73.1	-37.2
C12MOPA	136.0	111.4	-24.6

^aTheoretical $T_c(T_1)$ is the clearing (isotropization) temperature of the blend without interactions, i.e. $T_1 = T_{c1} \times X_1 + T_{c2} \times X_2$ where T_{c1} and T_{c2} are clearing temperatures of proton donor and proton acceptor, respectively, and X_1 (molar ratio of proton donor) = X_2 (molar ratio of proton acceptor) = 0.5. The isotropization temperatures of proton acceptors [28] are: C12P (88.8°C), C12M (84.0°C), C12PO (138.3°C) and C12MO (129.6°C).

^bExperimental $T_c(T_2)$ is the clearing (isotropization) temperature of the complex with hydrogen-bonded interactions.

^c ΔT is the deviation temperature of the experimental isotropization temperature (T_2) minus the theoretical isotropization temperature (T_1), i.e. $\Delta T = T_2 - T_1$.

N-oxide systems should have large T_c values by virtue of the stronger dipoles of their constituents; nevertheless, the molecular structures (shapes) of these supramolecular complexes cause the reverse effect on the deviation temperatures (ΔT). Importantly, the hydrogen-bonded cores are more highly kinked by insertion of an oxygen atom into their hydrogen bonds, by comparison with their non-oxide analogues. However, the trend MPA ($T_2 = 70.2^\circ\text{C}$; $\Delta T = -43.0^\circ\text{C}$) < MOPA ($T_2 = 111.4^\circ\text{C}$; $\Delta T = -24.6^\circ\text{C}$) is opposite to the former results; this can be attributed to a major contribution from their molecular structures rather than from their dipolar effects. In consequence, both the higher deviation temperatures (ΔT) and higher clearing temperatures (T_2) of MOPA may be produced by their more linear structures (see figure 4) compared with those of MPA. Overall, structural shape has a more dominant influence on phase behaviour than does the dipolar effect in these supramolecular complexes.

In comparing the non-oxide systems, ΔT values are in the following order: PPA (the most linear structure, $\Delta T = +36.4^\circ\text{C}$) > PMA (kinked between the core and the flexible part, $\Delta T = -2.2^\circ\text{C}$) > MPA (kinked in the rigid core bearing the H-bond, $\Delta T = -43.0^\circ\text{C}$). This reveals that various nonlinear shapes may be detrimental to the packing of the liquid crystalline or crystalline phases in different ways. For the bend structures in this series, the molecular structure kinked between core and flexible part (PMA) has a greater effect in sustaining a

higher clearing temperature (i.e. less reduction of ΔT in this bending site) than does the molecular structure kinked in the rigid core bearing the H-bond (MPA). In addition, the order of the clearing temperatures (T_2) and that of the deviation temperatures (ΔT) are similar in all complexes except PMA (the 4th rank in T_2 and the 2nd rank in ΔT). Based on the modified ΔT data, PMA (kinked between the core and the flexible part) has the least reduction in ΔT of all systems except the most linear system PPA. None the less, *N*-oxide systems shown in figure 4 do not have the same trend in ΔT values as in the former (non-oxide) comparison. ΔT values of *N*-oxide systems are as follows: POPA (kinked in the rigid core bearing the H-bond, $\Delta T = -9.6^\circ\text{C}$) > MOPA (linear shape with broadening cores, $\Delta T = -24.6^\circ\text{C}$) > POMA (linear shape with broadening cores and double kinks; one kink between the core and the flexible part, the other kink in the rigid core bearing the H-bond, $\Delta T = -37.2^\circ\text{C}$). Both the XRD results and the clearing temperatures (table 4) suggest that the schematic structures of *N*-oxide systems may not be so exact as drawn in figure 4. Hence, the reason for the largest ΔT and large *d*-spacing of POPA in *N*-oxide systems is still not clear. It may be possible that *N*-oxide systems have strong hydrogen bonds, or that the oxygen atom provides an additional lone pair of electrons (as the proton acceptor) for the hydrogen bonds. Overall, the *N*-oxide proton acceptors provide not only an extra choice of different polarities to induce stronger H-bonding, but also various combinations for various shapes of supramolecules.

In order to consider whether mesomorphism can be preserved in angular supramolecules for the kink moved two rings away from the H-bond (bending position 1 in figure 1), 1:1 complexes of *trans*-3-alkoxy-3'(or 4')-stilbazoles (or their analogous *N*-oxides) and 3(or 4)-decyloxybenzoic acid have been prepared [32]. These include the angular complex C_n MSPA formed by blending *trans*-3-alkoxy-4'-stilbazoles and 4-decyloxybenzoic acid as bending position 1 of figure 1. Their mesogenic properties are much worse than the previous supramolecules, i.e. no SmA or SmC phases are observed. This indicates that if the bending site is moved far away from the H-bond, the angular mesogenic packing efficiency will not be recovered easily through the flexible H-bond; angular supramolecules can thus sustain better mesomorphism with the bending positions close to the H-bond.

In conclusion, the influence of structural nonlinearity on mesogenic properties can be generalized as follows. Lower mesogenic transition temperatures and monotropic mesogenic phases are favoured in angular structures; moreover, bend structures may show new or broader mesogenic phases in comparison with their linear

isomeric structures. This work demonstrates that kinked structures provide a means of manipulating the mesomorphic properties of complexes using angular hydrogen-bonded interactions. Consequently, the structural shapes of supramolecules have a dominant influence on phase behaviour. Above all, we have successfully introduced unconventional mesomorphism by bending supramolecules at different kinked positions, rather than, traditionally, only by changing the length of the flexible part or by branching the rigid core. These results provide a new approach to the design of useful liquid crystalline materials.

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Appendix

In the complexes, H-bonded acceptors are *trans*-4-alkoxy-3'-stilbazole C_nM (1) or *trans*-4-alkoxy-4'-stilbazole C_nP (2) ($n=8, 12, \text{ and } 16$; where n is the carbon number of the alkoxy chain), or their analogous *N*-oxides C_nMO (3) and C_nPO (4); H-bonded donors are 3-decyloxybenzoic acid MA (5) or 4-decyloxybenzoic acid PA (6). The syntheses of *trans*-4-alkoxy-3'(or 4')-stilbazole and 3(or 4)-decyloxybenzoic acid are given below.

The synthesis of *trans*-4-alkoxy-3'(or 4')-stilbazole C_nM (1) and C_nP (2) (and their analogous *N*-oxides C_nMO (3) and C_nPO (4)) are described in the literature [28].

A general procedure for the preparation of 3(or 4)-decyloxybenzoic acid is as follows. Hydroxybenzoic acid (5 g, 36 mmol) and KOH (5 g, 90 mmol) were dissolved in ethanol-water (200 ml 9:1) and the solution stirred for 20 min. 1-Bromo-decane (16 g, 72 mmol) was then added and the mixture heated under reflux for 15 h. When the reaction was complete, KOH (2 g, 36 mmol) was added and the mixture heated under reflux for a further 3 h. The ethanol was evaporated off, and the mixture poured into water and acidified to approximately pH 5 with concentrated HCl. The precipitate was filtered, washed with water and hexane and recrystallized from hexane. Yield 85–90%. The results of 1H and ^{13}C NMR spectra and elemental analyses are as follows:

3-Decyloxybenzoic acid, MA (5) 1H NMR δ ($CDCl_3$) 0.89 (t, 3H, CH_3), 1.28–1.46 (m, 14H, $7 \times CH_2$), 1.73–1.87 (m, 2H, CH_2), 4.01 (t, 2H, OCH_2), 4.73 (s, 1H, $COOH$), 7.15 (d, 1H, $J=7.6$ Hz, Ar-H), 7.37 (t, 1H, Ar-H), 7.62 (s, 1H, Ar-H), 7.71 (d, 1H, $J=7.7$ Hz, Ar-H). ^{13}C NMR δ ($CDCl_3$) 14.10, 22.67, 26.00, 29.17, 29.31, 29.36, 29.56, 31.89, 68.27, 115.07, 120.91, 122.45, 129.45, 130.48, 159.18,

172.03. Elemental analysis: calculated C 73.35, H 9.41; experimental C 73.38, H 9.29%.

4-Decyloxybenzoic acid, PA (6) 1H NMR δ ($CDCl_3$) 0.88 (t, 3H, CH_3), 1.26–1.45 (m, 14H, $7 \times CH_2$), 1.74–1.87 (m, 2H, CH_2), 4.02 (t, 2H, OCH_2), 6.93 (d, 2H, $J=8.9$ Hz, $2 \times Ar-H$), 8.05 (d, 2H, $J=8.8$ Hz, $2 \times Ar-H$). ^{13}C NMR δ ($CDCl_3$) 14.10, 22.67, 25.97, 29.08, 29.30, 29.34, 29.54, 31.89, 68.29, 114.18, 121.39, 132.32, 163.69, 172.00. Elemental analysis: calculated C 73.35, H 9.41; experimental C 73.28, H 9.67%.

Hydrogen-bonded donor and acceptor moieties were identified as the required materials and judged to be pure by 1H and ^{13}C -NMR spectroscopy. Elementary analytical results for C, H and N are also satisfactory [28]. Hydrogen-bonded complexes were prepared by slow evaporation from THF solution containing the mixtures of a 1:1 molar ratio of the H-bonded donor and acceptor moieties, followed by drying *in vacuo* at 60°C.

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