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Preparation and liquid crystalline properties of a new type of hydrogen-bonded liquid crystals containing an aryl-acetylene moiety

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A new type of liquid crystals formed through hydrogen bonding between 4-alkoxybenzoic acids and 4-alkoxyphenylethynylpyridines have been investigated by differential scanning calorimeter and polarizing optical microscopy. These materials show a typical nematic phase.

1. Introduction

Non-convalent interactions between dissimilar molecules, such as hydrogen bonds, dipole–dipole interactions and π–π interactions, have been a useful tool in designing new supramolecular materials. Among these, hydrogen bonding plays an important role in molecular recognition and self-assembly because of its stability, and directionality [1]. In recent years, the study of thermotropic liquid crystals induced by intermolecular hydrogen bonding between different species has attracted considerable interest since Kato and co-workes showed that hydrogen bonding between 4-alkoxybenzoic acids and pyridine derivatives was responsible for the formation of liquid crystal phases [2, 3]. Only a few types of compounds containing ethylene, ether or azo groups have been reported as either hydrogen bond acceptors or donors despite the large number of supramolecular hydrogen-bonded liquid crystals reported over the last few years [4–10]. In order to understand fully the relationships between the liquid crystalline properties of such mixtures and the structures of the components, we need to prepare new types of hydrogen-bonded liquid crystals. High birefringence (Δn) liquid crystals are useful materials for application in reflective-type LCDs, spatial light modulators, compensation film reflectors and polarizers [11–14]. Liquid crystals containing aryl-acetylene groups exhibit high birefringences, low viscosities and low melting points. Thus, liquid crystals containing the aryl-acetylene moiety have been widely used in many areas. Recently we reported the first aryl-acetylene-containing liquid crystal formed by intermolecular hydrogen bonding.

In this paper, we report the preparation and liquid crystalline properties of 10 supramolecular liquid crystals formed by intermolecular hydrogen bonding between 4-alkoxybenzoic acids and 4-alkoxyphenylethynylpyridines (scheme 1). We compare the properties of these complexes with those of other types of hydrogen-bonded liquid crystals and discuss the relationship between the liquid crystalline properties and the molecular structures.

2. Experimental

2.1. *Synthesis of BAn Compounds*

BA*n* Compounds were prepared by heating 4-hydroxybenzoic acid with the corresponding bromoalkane at reflux in a KOH ethanol solution, with subsequent acidification. The BA*n* compounds were characterized by mass spectroscopy and elemental analysis [4, 10].

2.2. *Synthesis of PEP5 and PEP6*

PEP5 and PEP6 were prepared by the method shown in scheme 2. The procedures are summarized below [15].

2.2.1. *4-Bromophenol*

To a solution of phenol (100 g) in CS_2 (100 ml) below 5°C, a bromine (55 ml) solution in CS_2 (50 ml) was added over a 2 h period. The solvent was then removed by rotary evaporation and the residue was fractionally distilled (b.p. = 141–145°C/25 mm Hg) to yield 153 g of colourless crystals; m.p. 63°C, yield 80%.

2.2.2. *4-Hexyloxy-4′-bromobenzene*

Water (10 ml) and K_2CO_3 (12.5 g, 0.09 mol) were added to a solution of 4-bromophenol (2.85 g, 0.01 mol) in ethanol (90 ml) [16]. After heating the mixture to reflux, a solution of bromohexane (10.7 ml) in ethanol

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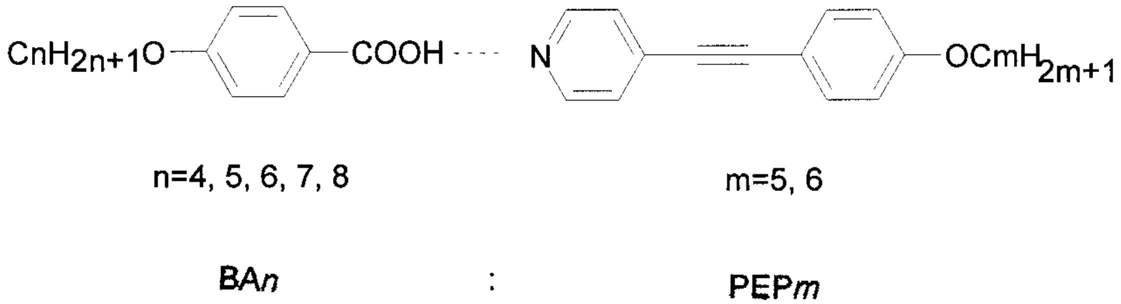
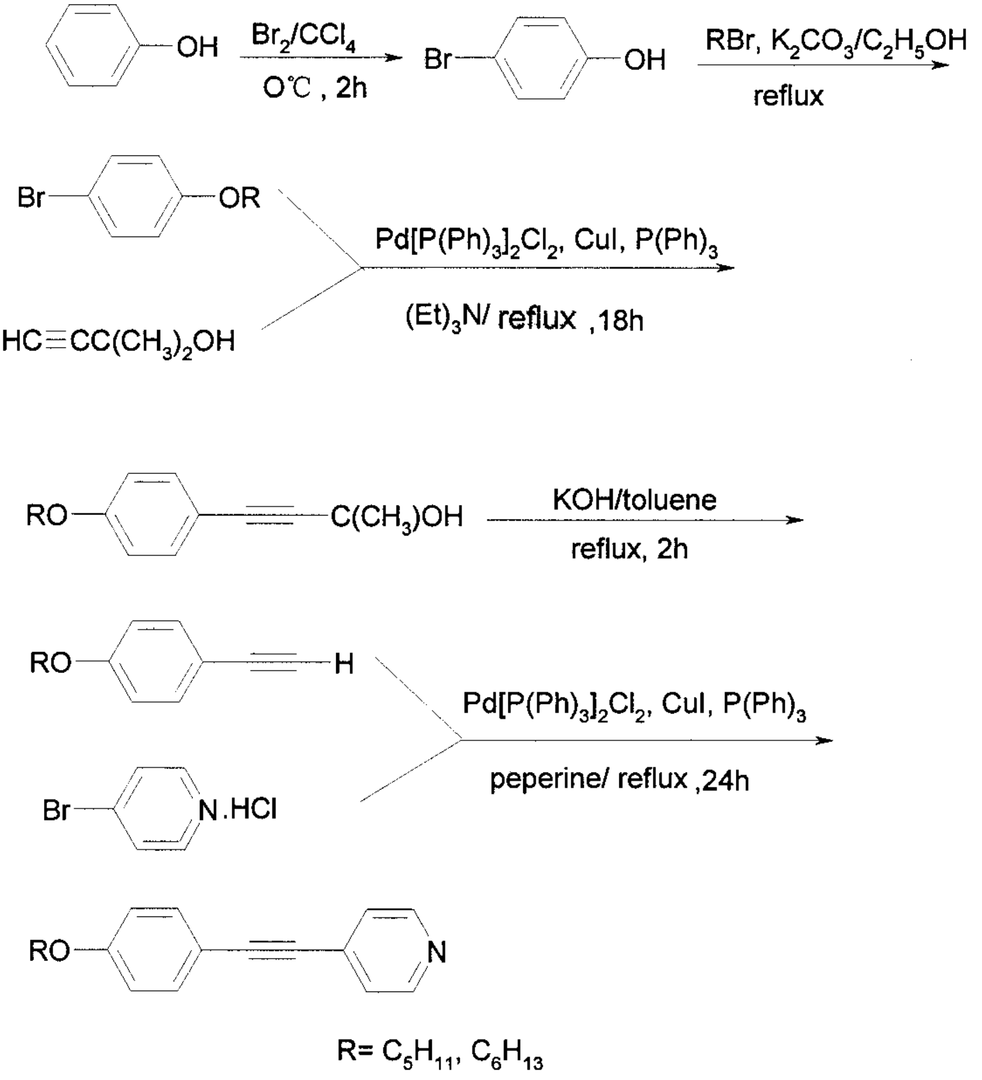


Scheme 1. Structures of BA*n* and PEP*m* compounds.

(60 ml) was added dropwise. The solution was heated under reflux for 18 h; it was then cooled, filtered, and the solvent was removed by rotary evapouration to yield a colourless liquid. Pure 4-hexyloxy-4′-bromobenzene was obtained by fractional distillation (b.p. = 140–143°C/5 mm Hg); yield 79%.

2.2.3. *4-(4-Hexyloxy)phenyl-2-methyl-3-butyn-2-ol*

To a solution of 4-hexyloxy-4′-bromobenzene (2.57 g, 0.01 mol) and 2-methyl-3-butyn-2-ol (0.92 g, 0.011 mol) in triethylamine (15 ml), under nitrogen, were added CuI (20 mg), Pd[PPh_3]$_2$$Cl_2$ (20 mg) and PPh_3 (40 mg). The solution was heated at reflux for 8 h. After cooling,



Scheme 2. Synthetic route to PEP5 and PEP6.

the mixture was filtered and washed with ether (25 ml). The filtrate was evapourated to remove the solvent; the residual orange oil was dissolved in chloroform (50 ml) and washed three time with water (50 ml) and 5% aqueous HCl. The organic layer was dried over $MgSO_4$ overnight, filtered and the solvent was evapourated. The residue was purified by column chromatography on silica gel (petroleum/dichloromethane = 4/1 as the eluent); yield 60%.

2.2.4. *4-Hexyloxyphenylactylene*

A solution of 4-(4-hexyloxy)phenyl-2-methyl-3-butyn-2-ol in toluene (40 ml) was placed in a flask with KOH (0.5 g, 0.0084 mol). The mixture was heated at reflux for 3 h, it was then cooled, filtered, and the filtrate was evapourated to remove toluene. The residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 2/1 as the eluent) to yield a light yellow oil; yield 60%.

2.2.5. *PEP5 and PEP6*

For the synthesis of PEP5, CuI (40 mg), $Pd[PPh_3]_2Cl_2$ (40 mg) and PPh_3 (160 mg) were added to a solution of 4-hexyloxyphenylactylene in triethylamine. The solution was heated at reflux for 24 h. After filtration, the solvent was removed by rotary evourparation to yield an orange residue. This residue was dissolved in chloroform (50 ml) and the solution washed three times with water (50 ml). The organic layer was separated and dried over $MgSO_4$ overnight. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 2/1 as the eluent) to give a colourless solid; yield 70%. PEP6 was synthesized by an analogous method.

PEP5: m.p. 39.5–40.6°C, *M/z*: 265. Elemental anylysis: calc. for $C_{18}H_{19}O_1N_1$ C 81.48, H 7.22, N 5.28; found C 81.40, H 7.087, N 5.163% ^{1}H NMR (400 MHz) ($CDCl_3$, ppm): 8.584(2H, d, $J = 5.92$ Hz) and 7.358(2H, d, $J_1 = 5.92$ Hz, $J_2 = 1.44$ Hz) (pyridyl), 7.489(2H, d, $J = 5.68$ Hz) and 6.904(2H, d, $J = 7.00$ Hz) (phenyl), 3.980(2H, t, $J = 6.56$ Hz) (OCH_2), 1.766–1.837(2H, m) (OCH_2CH_2), 1.381–1.470(4H, m), 0.940(3H, t, $J = 7.10$ Hz) (CH_3).

Table 1. Transition temperatures (°C) of the BA*n* series.

Compound	Phase transition
BA4	Cr 147 N 160 I
BA5	Cr 124 N 151 I
BA6	Cr 106 N 153 I
BA7	Cr 92 SmC 98 N 146 I
BA8	Cr 97 SmC 122 N 143 I

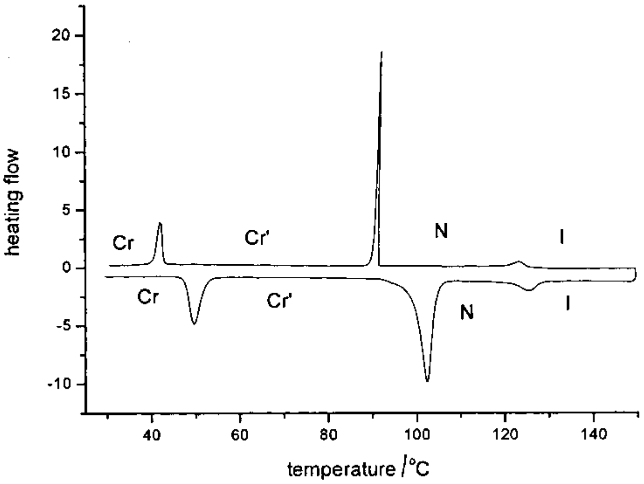
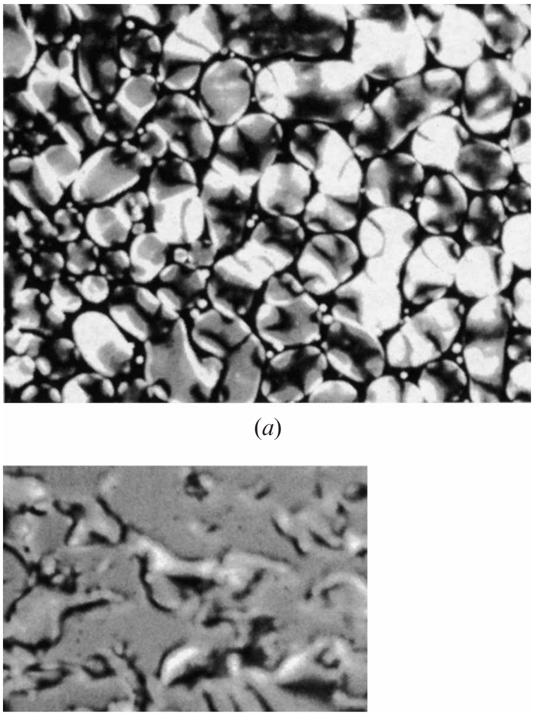


Figure 1. DSC traces for the complex BA5: PEP5.

PEP6: m.p. 38.7–39.4°C, *M/z*: 279. Elemental anylysis calc. for $C_{19}H_{21}O_1N_1$ C 81.68, H 7.58, N 5.01; found C 81.66, H 7.513, N 4.909%. ^{1}H NMR (400 MHz) ($CDCl_3$, ppm): 8.585(2H, d, $J = 5.64$ Hz) and 7.357(2H, d, $J_1 = 6.00$ Hz, $J_2 = 1.6$ Hz) (pyridyl), 7.489(2H, d, $J = 4.76$ Hz) and 6.904(2H, d, $J = 7.16$ Hz) (phenyl), 3.980(2H, t, $J = 6.56$ Hz) (OCH_2), 1.773–1.828


(*a*)

(*b*)

Figure 2. Optical textures of the complex BA7: PEP5: (*a*) 120°C (heating) droplets texture; (*b*) 106°C (cooling) schlieren texture.

(2H, m)(OCH$_2$*CH*$_2$), 1.380–1.465(4H, m), 0.930(3H, t, J=7.05 Hz) (CH$_3$).

2.3. *Preparation of the hydrogen-bonded complexes*

All the hydrogen-bonded complexes were obtained by evaporation from their THF solution containing equal molar quantities of the H-bonding donor and the H-bonding acceptor compounds, followed by drying in vacuum at room temperature.

3. Results and discussion

3.1. *FTIR study*

The presence of intermolecular hydrogen bonding in the complexes formed between BA*n* and PEP*m* was confirmed by the observation of bands centred at 2450, and 1950 cm^{-1} in the IR Spectra associated with the N...H–O hydrogen bond, and the absence of the band centred at 3000 cm^{-1} which is observed for the carboxylic acid dimer(C–O...HO).

3.2. *Mesomorphic properties*

PEP5 and PEP6 are not liquid crystalline and melt directly to the isotropic liquid at 39.5–40.6°C and 38.7–39.4°C, respectively. All BA*n* compounds exhibit liquid crystalline phases. BA4, BA5 and BA6 are nematic liquid crystals; BA7 and BA8 show smectic and nematic phases. The thermal properties of the BA*n* series are shown in table 1. These temperatures are in good agreement with literature values [17].

The thermal behaviour of the hydrogen-bonded complexes (see figure 1) as characterized by differential scanning calorimetry (DSC). Polarizing optical microscopy (POM) was used to identify the liquid crystalline phases. The thermal behaviour of all the complexes is

Table 2. Transition temperatures (°C) and associated enthalpy changes (J g^{-1}) of the hydrogen-bonded complexes.

Complex	Phase transitions
BA4: PEP5	$\mathrm{Cr} \underset{98.0(54.2)}{\overset{108.6(52.6)}{\rightleftharpoons}} \mathrm{N} \underset{124.1(4.3)}{\overset{127.1(5.8)}{\rightleftharpoons}} \mathrm{I}$
BA5: PEP5	$\mathrm{Cr} \underset{41.9(21.3)}{\overset{49.6(23.1)}{\rightleftharpoons}} \mathrm{Cr'} \underset{92.3(58.6)}{\overset{102.4(61.3)}{\rightleftharpoons}} \mathrm{N} \underset{123.2(5.4)}{\overset{125.3(6.4)}{\rightleftharpoons}} \mathrm{I}$
BA6: PEP5	$\mathrm{Cr'} \underset{77.8(70.1)}{\overset{91.1(76.7)}{\rightleftharpoons}} \mathrm{N} \underset{124.6(4.7)}{\overset{126.4(6.0)}{\rightleftharpoons}} \mathrm{I}$
BA7: PEP5	$\mathrm{Cr} \xrightarrow{59.1(42.4)} \mathrm{Cr'} \xrightarrow{88.9(57.7)} \mathrm{N} \underset{117.9(6.1)}{\overset{120.1(6.1)}{\rightleftharpoons}} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[71.3(54.6)]{} \mathrm{N}$
BA8: PEP5	$\mathrm{Cr} \xrightarrow{59.5(42.9)} \mathrm{Cr'} \xrightarrow{89.2(56.9)} \mathrm{N} \underset{117.4(4.7)}{\overset{120.9(4.6)}{\rightleftharpoons}} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[71.3(54.6)]{} \mathrm{N}$
BA4: PEP6	$\mathrm{Cr} \xrightarrow{73.9(44.2)} \mathrm{Cr'} \xrightarrow{94.7(47.8)} \mathrm{N} \underset{129.2(5.2)}{\overset{130.2(6.1)}{\rightleftharpoons}} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[84.5(44.9)]{} \mathrm{N}$
BA5: PEP6	$\mathrm{Cr} \xrightarrow{82.3(19.2)} \mathrm{Cr'} \xrightarrow{95.0(42.7)} \mathrm{N} \underset{125.0(5.6)}{\overset{127.0(6.0)}{\rightleftharpoons}} \mathrm{I}$ $\mathrm{Cr} \xleftarrow[85.8(43.9)]{} \mathrm{N}$
BA6: PEP6	$\mathrm{Cr} \underset{66.1(4.0)}{\overset{70.1(5.1)}{\rightleftharpoons}} \mathrm{Cr'} \underset{87.6(70.3)}{\overset{103.3(79.0)}{\rightleftharpoons}} \mathrm{N} \underset{126.9(5.6)}{\overset{128.4(6.3)}{\rightleftharpoons}} \mathrm{I}$
BA7: PEP6	$\mathrm{Cr'} \underset{76.6(59.6)}{\overset{96.5(64.2)}{\rightleftharpoons}} \mathrm{N} \underset{119.8(6.0)}{\overset{122.3(6.4)}{\rightleftharpoons}} \mathrm{I}$
BA8: PEP6	$\mathrm{Cr'} \underset{76.4(63.5)}{\overset{97.2(69.9)}{\rightleftharpoons}} \mathrm{N} \underset{122.6(6.3)}{\overset{124.8(6.8)}{\rightleftharpoons}} \mathrm{I}$

very different from those of the corresponding H-bond donor and acceptor. This confirmed the presence of strong hydrogen bonding between the components. On cooling the mixtures from the isotropic liquid, droplets were observed which coalesced to form a schlieren texture (figure 2). All the complexes were liquid crystalline and exhibited an enantiotropic nematic phase. The DSC thermogram for the complex BA5: PEP5 is shown in figure 1. Figure 2 gives optical textures for BA7: PEP5. The thermodynamic data for the mixtures are summarized in table 2.

As with other types of aryl-acetylene-containing liquid crystals, these hydrogen-bonded complexes have low viscosities. It was noted that most of the corresponding hydrogen-bonded complexes exhibited smectic phases when the acetylene bond was replaced by double bonds such as –N = N–, –C = N– and –C = C– [4, 6, 10, 18, 19]. When the acetylene group was replaced by an azo linkage, the corresponding phenyl-pyridines PAP*m* were not mesogenic; however, the complexes BA*n*: PAP*m* all show an enantropic smectic phase [20]. Most of the corresponding phenyl-pyridines containing either –C = C– (*n*PhVPy) or –C = N– (sz) linkage, are liquid crystals. The complexes BA*n*: *n*PhVPy and BA*n*: SZ all show a smectic phase and some also show a nematic phase.

On increasing the chain length of the 4-alkoxybenzoic acids, the melting points of BA*n*: PEP5 decrease and the temperature range of the phase becomes wide (see figure 3). It is interesting to note that the clearing points of the BA*n*: PEP5 complexes exhibit an odd–even effect. BA5: PEP5, BA7: PEP5 and BA8: PEP5 exhibit also a crystal–crystal phase transition.

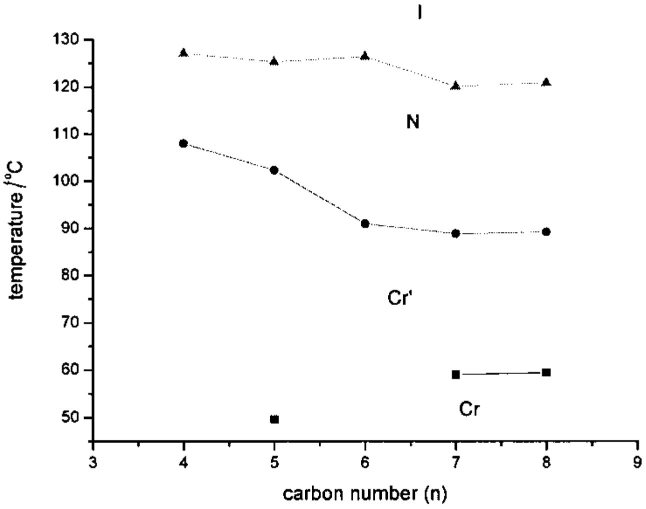


Figure 3. Plot of transition temperatures against the BA*n* chain length for the 1 : 1 hydrogen-bonded complexes, BA*n*: PEP5.

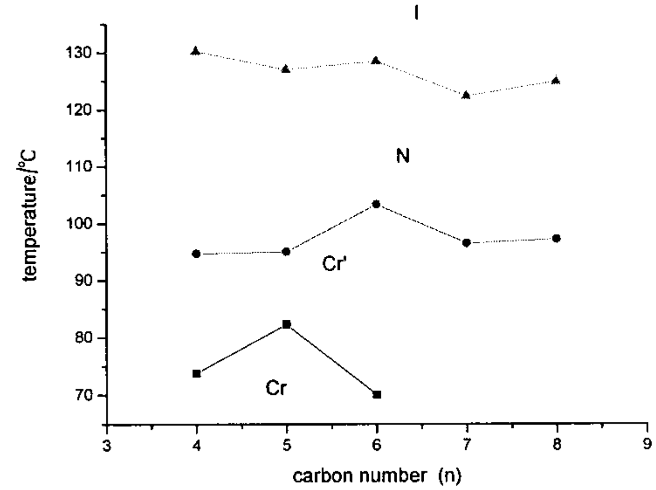


Figure 4. Plot of transition temperatures against the BA*n* chain length for the 1 : 1 hydrogen-bonded complexes, BA*n*: PEP6.

As for the BA*n*: PEP6 complexes, increasing the length of the terminal chain on the 4-alkoxybenzoic acid has little effect on the melting point except for BA6: PEP6 (see figure 4). The odd–even effect is apparent however, in their clearing points. There is a crystal–crystal phase transition for the BA4: PEP6, BA5: PEP6 and BA6: PEP6 complexes.

The clearing point of a BA*n*: PEP6 mixture is a little higher than that of the corresponding BA*n*: PEP5 complex. For example, the clearing points of BA4: PEP6 and BA4: PEP5 are 130.2°C, and 127.1°C, respectively. On increasing the length of the chain in BA*n*, the nematic range of BA*n*: PEP5 becomes larger while the opposite is observed for the BA*n*: PEP6 Mixtures.

4. Conclusion

Supramolecuar hydrogen-bonded liquid crystals containing an aryl-acetylene group have been prepared; their liquid crystalline properties were studied and compared with other types of hydrogen-bonded liquid crystals. All the complexes showed a stable nematic liquid crysal phase and there was an odd–even effect in their clearing points on varying the length of the chain in the acid component. These liquid crystals have application potential as a new type of high birefringence liquid crystals for use in many areas. This work provides important data for understanding the relationships between the liquid crystalline properties and the molecular structures in hydrogen-bonded liquid crystals.

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