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Symmetric bi-pyridyl banana-shaped molecule and its intermolecular hydrogen bonding liquid-crystalline complexes

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1. Introduction

Banana-shaped liquid crystals have attracted much attention since Niori et al. first reported in 1996 because they exhibit a variety of unique phases and respond as ferroelectric and antiferroelectric materials [1]. These banana-shaped molecules can give rise to a number of different mesophases provisionally labeled as B phases and this nomenclature express the special features of the liquid-crystalline phases formed by the banana-shaped molecules. Until now, liquid-crystalline phases B₁–B₈ [2,3] were found. Among them, B₂, B₅ and B₇ are switchable by applied electric field [4] while B₄ phase is designated as the 'blue phase' [5]. The B₂ is the most common and the most widely studied phase. This tilted lamellar polar phase can appear in four different supramolecular packing arrangements, two of which form chiral conglomerates and two of which appear as racemates [6-8]. In recent years, however, increasing research activity has focused on materials in which the bent core is assembled via hydrogen bonding interactions.

Hydrogen bonding is one of the key interactions for chemical and biological processes in nature due to its stability, directionality, and dynamics. The intermolecular hydrogen bonding between carboxyl and pyridyl moieties has been found to be extremely fruitful for the formation of liquid crystals [9–11]. The hydrogen bonding liquid crystal of rod shaped is investigated in detail by Kato and Frechet [12,13]. The first hydrogen bonding bananashaped liquid crystal is reported by Gimeno et al. [14]. They proved that it is possible to stabilize this type of mesophase through

ABSTRACT

A new symmetric bi-pyridyl banana-shaped molecule 1,3-phenylene diisonicotinate (PDI) was designed and synthesized. Its molecular structure was confirmed by FTIR, Elemental analysis and ¹H NMR. X-ray crystallographic study reveals that there is an angle of approximate 118° among the centroids of the three rings (pyridyl-phenyl-pyridyl) in each PDI molecule indicating a desired banana shape. In addition, a series of liquid crystal complexes nBA:PDI:nBA induced by intermolecular hydrogen bonding between PDI (proton acceptor) and 4-alkoxybenzoic acids (nBA, proton donor) were synthesized and characterized. The mesomorphism properties and optical textures of the complex of nBA:PDI:nBA were investigated by differential scanning calorimetry, polarizing optical microscope and X-ray diffraction.

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hydrogen bonding interactions. Recently, another symmetric or unsymmetric hydrogen bonded banana-shaped liquid crystal materials have been investigated by Martin and Bruce [15].

Here, we report a novel series of hydrogen bonding bananashaped liquid crystals in which 1,3-disubstituted benzene with 4-pyridine connected via ester linkages instead of the two Schiff's base-containing units [16]. In this supramolecular complex, the symmetric bent core 1,3-phenylene diisonicotinate (PDI) has no mesophase and it acts as the proton acceptor, while 4-alkoxybenzoic acids (nBA) act as the proton donor and the series of nBA show different mesophase such as smectic C or nematic. After introducing the hydrogen bonding interactions between PDI and nBA, the complexes nBA:PDI:nBA show the typical B phase of bananashaped liquid crystals.

2. Experimental

2.1. Synthesis

The PDI was prepared by resorcinol (0.1 mol) and isonicotinic acid (0.2 mol) which were dissolved in dry dichloromethane with dicyclohexylcarbodiimide (DCC) (0.22 mol). The mixture was stirred at room temperature for about 48 h. The product was purified by flash chromatography on silica gel using chloroform/methanol (20:1) as eluent, and then recrystallized three times from ethanol to provide a white crystalline solid. Yield: 30%. ¹H NMR for PDI shown in Fig. 1 (DMSO, ppm): 8.89 (d, 4H, *J* = 6.0 Hz); 8.02 (d, 4H, *J* = 6.0 Hz); 7.60 (t, 1H, *J* = 8.2 Hz); 7.43 (s, 1H); 7.35 (d, d, 2H, *J* = 8.2, 2.2 Hz). Elemental analysis for C₁₈H₁₂N₂O₄: calcd C 67.50, H 3.78, N 8.75; found C 67.67,





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Fig. 1. ¹H NMR spectrum of PDI (DMSO).

H 3.89, N 8.72%. The 4-alkoxybenzoic acids (nBA) were prepared according to literature methods [17]. The complex nBA:P-DI:nBA were prepared by dissolving 1:2 molar amount of PDI and nBA in anhydrous pyridine and evaporating pyridine slowly under reduced pressure. The complexes were dried under vacuum for at least 24 h before characterizations [18].

2.2. Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary data under deposition number CCDC 634149. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033; e-mail: data_request@ccdc.cam.ac.uk].

2.3. Characterization

¹H NMR spectrum was recorded on a Bruker Avance 500 instrument using CDCl₃ as solvent and TMS as internal reference. Elemental analysis (C, H and N) were performed on a Flash EA1112 from ThermoQuest Italia S.P.A. Fourier transform infrared (FTIR) spectra were recorded on a BRUKER IFS-66V equipped with a DTGS detector. The spectra were collected with a 4 cm⁻¹ resolution and at room temperature. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204. The DSC analysis was carried out at rates of 5 °C/min by applying several heating and cooling cycles from 40 to 140 °C. Optical textures were observed by a Leica DMLP polarizing optical microscope equipped with a Leitz 350 microscope heating stage. Variable-temperature XRD experiments were performed on a Rigaku X-ray diffractometer (Dmax 2500 V, using CuKa1 radiation of a wavelength of 1.54 Å) with a PTC-20A temperature controller.

As for the X-ray Diffraction, diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan technique with graphite-monochromated MoK α (λ = 0.71073 Å) radiation. The structures were solved by direct methods and refined by the fullmatrix least-squares technique using the SHELXTL programs. Anisotropic displacement parameters were applied to all nonhydrogen atoms, hydrogen atoms were assigned isotropic displacement coefficients.

3. Result and discussion

3.1. Synthesis of the PDI

The synthetic route for the proton acceptor PDI and the structures of nBA and the complexes nBA:PDI:nBA are illustrated in Scheme 1. The chemical structure of PDI is confirmed by FTIR, Elemental analysis and ¹H NMR (Fig. 1).



Scheme 1. Chemical structures of the PDI, nBA and nBA:PDI:nBA.

3.2. X-ray crystallographic analysis of the PDI

The PDI (0.032 g, 0.1 mmol) was dissolved in a solution of ethanol (5 ml) and was allowed to evaporate slowly at room temperature. Colorless crystals of PDI were obtained after one week.

The crystal structure of PDI is exhibited in Fig. 2. Systematic absences in the diffraction data of PDI establish the space group as *P*-1. The crystal details are summarized in Table 1. The main intermolecular interactions in the crystal are weak hydrogen bonds including C–H···N (pyridyl) and C–H···O (carbonyl) which are exhibited in Fig. 2. It is noticeable that there is an angle of approximate 118° among the centroids of the three rings (pyridyl–phe-nyl–pyridyl) in each PDI molecule which indicating a desired banana shape.

3.3. Intermolecular hydrogen bonding of the complex nBA:PDI:nBA

In order to confirm the intermolecular hydrogen bonding between the PDI and nBA, we choose FTIR spectroscopy because it is sensitive to the change of molecular conformation, inter and intramolecular interactions [19,20]. The FTIR spectra of PDI, 12BA, and 12BA:PDI:12BA are shown in Fig. 3. The peak of the carboxylic carbonyl band of 12BA is 1687.0 cm⁻¹, this band shows that the carboxylic acid dimer occurs by means of intermolecular hydrogen bonding [21]. The spectrum of PDI has an ester carbonyl band at 1747.3 cm⁻¹. In the IR spectrum of complex 12BA:PDI:12-BA, the ester carbonyl band changes from 1747.3 cm^{-1} to 1751.1 cm⁻¹ due to the complexation of PDI with nBA, and the carboxylic carbonyl peak changes from 1687.0 cm^{-1} of $(nBA)_2$ to 1695.2 cm⁻¹. These results mean that the intermolecular hydrogen bonding between carboxylic acids has been substituted by the intermolecular hydrogen bonding between the pyridyl and the carboxylic acid, especially the two new bands centered at 2537.0 cm⁻¹ and 1911.0 cm⁻¹ can been seen very clearly. These two new bands are strong evidence of the intermolecular hydrogen bonding, which is of an unionized type between the pyridyl and the carboxylic acid [22,23]. The other complexes of the nBA:PDI:n-BA show the same characteristic in FTIR spectra. Furthermore, the

Table 1

Crystallographic data for compound PDI

Formula	$C_{18}H_{22}N_2O_4$
Formula weight	320.30
Temperature	293(2) K
Space group	P-1
a (Å)	7.9838(16)
b (Å)	12.279(3)
c (Å)	30.891(6)
α (°)	89.70(3)
β (°)	90(3)
γ (°)	90(3)
v (Å ³)	3028.3
Ζ	8
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	2.209
μ (cm ⁻¹)	0.71
Crystal size (mm ³)	$0.053\times0.136\times0.371$
Color	Colorless crystal
$2\theta_{\max}$ (°)	55.55
Reflns meads	12975
Reflns used (R_{int})	8421 (11.6060)
Final $R[I > 2\sigma(I)]$	$R_1a = 0.0839, wR_2b = 0.1976$
R indices (all data)	$r_1 = 0.2888, wr_2b = 0.3151$
Goodness-of-fit on F^2	0.866

${}^{a}R_{1} = \sum |F_{0}| - |F_{C}| / \sum |F_{0}|.$

 ${}^{b}wR_{2} = \sum_{r} \sum_{w} (F_{0}^{2} - F_{C}^{2})2_{J} / \sum w(F_{0}^{2})2_{J} / 2; w = 1/\lceil \sigma 2(F_{0}^{2}) + (0.08P)2_{J}$ where $P = \lceil \max(F_{0}^{2}, 0) + 2F_{C}^{2} / 3.$

formation of the complex was easily confirmed through polarizing optical microscopy measurements; the solid samples melted cleanly without the appearance of biphasic regions, which would otherwise have indicated the presence of nonstoichiometric complexes.

3.4. Mesomorphic properties of the complexes nBA:PDI:nBA

The detailed phase behaviour of the PDI and complexes nBA: PDI:nBA were investigated by differential scanning calorimetry. The DSC curves of 10BA:PDI:10BA and 12BA:PDI:12BA on cooling are given in Fig. 4. The transition temperatures and enthalpies of these complexes are summarized in Table 2. From the results of





Fig. 3. FTIR spectra of compounds PDI, 12BA and 12BA:PDI:12BA at room temperature.



Fig. 4. The DSC thermograms of 10BA:PDI:10BA and 12BA:PDI:12BA on cooling.

Thermal	transitions	of	PDI	and	nBA:PDI:nBA	series

Table 2

Compound	Cooling ^{ab}				Heating				
	I	B_2		Cr	Cr		B_2	J	I
PDI		-	111.1(124.3)	-	-	143.3(122.6)	-		_
4BA:PDI:4BA		-	108.6(16.5)	-	-	120.5(16.0)	-		_
7BA:PDI:7BA	- 80.6(15.3)	-	52.4(22.8)	-	-	91.7(37.0)	-		_
8BA:PDI:8BA	- 84.8(25.2)	-	83.4(19.3)	-	-	90.4(13.6)	-	98.1(37.7) -	_
10BA:PDI:10BA	- 84.9(10.5)	-	72.3(38.2)	-	-	86.7(24.7)	-	94.5(27.5)	_
12BA:PDI:12BA	- 77.9(10.3)	-	68.2(14.4)	-	-	90.8(11.3)	-	92.3(9.17)	_

 a Phase transition temperatures (°C) and enthalpies of transition (kJ/mol) (in parentheses).

Cr, crystalline; B₂, smectic C polar mesophase; I, isotropic liquid phase.

DSC, we find the melting point of PDI is 143.3 °C and the bananashaped PDI has no mesophase, while the proton donor nBA has shown different mesophases such as smectic C or nematic phases [24]. The intermolecular hydrogen bonding induced complexes nBA:PDI:nBA show mesophases which are different from the ones of nBA. Among them, 4BA:PDI:4BA shows no liquid-crystalline phase with a single peak at 120.5 °C. With the increase of the alkoxy chain length, 7BA:PDI:7BA is monotropic and its liquid-crystalline phase is only observed during cooling process. The complexes of n = 8, 10, 12 in the series exhibit enantiotropic liquid-crystalline phases.

We also studied the phase transitions by polarizing optical microscopy to confirm the textures of the complexes. On the slow cooling from the isotropic liquid of this series complex, a texture with circular-domain can be found and it is the B₂ phase. This kind of fluid smectic phase was observed for most of the complexes. The polarizing photomicrographs of complexes 10BA:PDI:10BA and



Fig. 5. Optical textures of (a) 10BA:PDI:10BA on cooling at 75 °C (400×) and (b) 12BA:PDI:12BA on cooling at 70 °C (200×).



Fig. 6. X-ray diffraction pattern of complex 12BA:PDI:12BA at 75 °C on cooling.



Fig. 7. Chemical structures and the phase transitions of the molecules reported by Pelzl's group (temperatures in °C) [25].

12BA:PDI:12BA on cooling are given in Fig. 5a with magnification 400 and in Fig. 5b with magnification 200, respectively.

In order to identify the exact liquid phase, the X-ray diffraction of nBA:PDI:nBA at elevated temperatures is examined. Fig. 6 shows the X-ray diffraction of 12BA:PDI:12BA at 75 °C on cooling. In the small angle region a single sharp peak at 2θ of 2.78° was observed, whereas in the wide angle region there is a broad halo which is consistent with the diffuse lamellar structure. This result indicates a layer structure and the layer spacing *d* is 31.8 Å for the liquid-crystalline phase. The measured interlayer distance (31.8 Å) is significantly shorter than the calculated molecular length (51.6 Å) and indicating the tilted lamellar structure of the complex with angle of around 52.4°. All these facts are consistent with a B₂ mesophase in which 12BA:P-DI:12BA molecules are organized in layer structures and tilted.

We find an example of banana-shaped liquid crystals in the literature which could be considered as a covalent analogue of our bent complexes and compared the mesomorphic properties of nBA:PDI:nBA with the related liquid crystals reported by PelzI's group [25] (shown in Fig. 7). From the data obtained, we can conclude that both of the molecules show the B₂ phase, so it is successful to form banana-shaped liquid crystals through hydrogen bonding between pyridine and carboxyl. But the mesomorphic temperature of the covalent analogue is higher 20 °C than the nBA:PDI:nBA, so the intermolecular hydrogen bonding between PDI and nBA decreases the phase transition temperature because the hydrogen bonding is more flexible than the covalent bond.

4. Conclusions

In this paper, we designed and synthesized a symmetric banana-shaped molecule (PDI), and through the X-ray crystallographic analysis, the bent angle of PDI is confirmed as 118°. We take the symmetric PDI as the proton acceptor and nBA as the proton donor and get the symmetric banana-shaped complexes of nBA:PDI:nBA through intermolecular hydrogen bonding. The intermolecular hydrogen bonding interactions between PDI and nBA were confirmed by FTIR. The mesomorphism of the complexes was characterized through differential scanning calorimetry, polarizing optical microscope and X-ray diffraction measurements. The results are as follows: for the homologue with short terminal chains (n = 4), no liquid-crystalline phases were observed; the homologue with intermediate length of terminal chains (n = 7) exhibited monotropic liquid-crystalline phase, while ones with long terminal chains (n = 8, 10 and 12) displayed B₂ phases and they are all enantiotropic liquid crystals. In summary, intermolecular hydrogen bonding is a successful way to obtain different multifunctional banana-shaped liquid crystals.

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