

Banana Shape Liquid Crystal Studied by X-ray Diffraction (PXRD) Measurements

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Powder XRD Analyses of H-Bonded Asymmetric Heterodimers (with One H-Bond). (i) Four- and Five-Ring Systems (III n -Am, III n -Bm, and IV n -Am). The H-bonded molecular organizations of four- and five-ring asymmetric complexes in different mesophases (smectic phases) were investigated by XRD measurements (see Table 1). Wide-angle diffuse peaks corresponding to a d-spacing value of 4.6 Å indicated that similar liquidlike, in-plane orders with average intermolecular distances were prevalent inside the smectic layers of all H-bonded complexes. In addition, sharp XRD peaks indexed as (001) were observed at the corresponding d-spacing values of d_1 42.5, 46.1, 46.6, and 49.5 Å in small-angle regions of III12-A12, III12-A16, III16-A12, and III16-A16, respectively. The tilt angle values (between the molecular axis and the layer normal) were calculated from the values of d-spacing (d_1) and molecular length (L), where L is the theoretical coplanar molecular length from the molecular modeling. Almost equal values of d-spacing and calculated L were obtained in all complexes III n -Am (n, m 12 and 16), which revealed that LC molecules were nearly perpendicular to the plane surface. Hence, the XRD data supported the existence of the SmA phase, which was also verified by POM experiments to observe the fanlike and homeotropic textures.

The analogous XRD results also suggested the SmA phase for all complexes III n -Bm, which exhibited a single sharp reflection peak in the small-angle region with d_1 corresponding to the calculated L to prove the SmA phase. The detailed XRD data are illustrated in Table 5. With respect to complexes IV n -Am, sharp peaks indexed as (001) in the small-angle region were obtained at the associated d-spacing values of d_1 42.2, 47.6, 46.3, and 50.6 Å in IV12-A12, IV12-A16, IV16-A12, and IV16-A16, respectively. The tilt angles (θ) calculated from the values of d_1 and L were around 35–39°, and the tilt angles were normally larger than those of the SmC phase (without polar switching behavior), which has also been confirmed in previous reports. It is an indication that tilt lamellar arrangements existed in the mesophasic range of all complexes IV n -An. Therefore, the two-dimensional structures of the SmCP phase in complexes IV n -An were further confirmed by the XRD results.

TABLE 1: Phase Transition Temperatures and Enthalpies of H-Bonded Four- and Five-Ring Asymmetric Hetero-Dimers (with One H-Bond)^a

$H_{2n+1}C_6O$

III n-Am (x = 1)
III n-Bm (x = 2)

$H_{2n+1}C_6O$

IV n-Am

OC_nH_{2n+1}

Complex	n	m	x	Phase transition temperature/ ^a C [Enthalpy/kJ/g]
III12-A12	12	12	1	I 114.3 [20.5] SmA 71.2 [69.8] K
III12-A16	12	16	1	I 105.0 [14.0] SmA 70.4 [152.1] K
III16-A12	16	12	1	I 114.6 [25.0] SmA 69.1 [49.3] K
III16-A16	16	16	1	I 103.9 [14.3] SmA 80.6 [146.5] K
III12-B12	12	12	2	I 149.0 [7.5] SmA 99.0 [161.2] K
III12-B16	12	16	2	I 149.1 [9.6] SmA 96.3 [169.8] K
III16-B12	16	12	2	I 128.0 [10.8] SmA 91.2 [135.0] K
III16-B16	16	16	2	I 128.1 [8.2] SmA 96.2 [157.2] K
IV12-A12	12	12	—	I 99.2 [27.1] CmCP 91.7 [22.3] K
IV12-A16	12	16	—	I 96.5 [21.3] CmCP 86.9 [30.1] K
IV16-A12	16	12	—	I 88.2 [17.2] CmCP 75.0 [33.4] K
IV16-A16	16	16	—	I 119.0 [20.7] CmCP 103.7 [54.1] K

^a I = isotropic state; SmA = smectic phase with no (or less) tilt angle arrangements; SmCP = polar tilt smectic phase; K = crystalline state. The phase transitions were measured by DSC at the 2nd cooling scan with a cooling rate of 5 °C min⁻¹. Phase transitions of compound S12 were obtained as I 119.0 [22.5] CmCP 109.0 [41.9] K, which were reported by Pelzl et al.¹³

TABLE 5: XRD Data of H-Bonded Four- and Five-Ring Asymmetric Hetero-Dimers (with One H-Bond)

complex	measured spacing (d)/Å	Miller index	theoretical length (L)/Å	tilt angle/°
III12-A12	42.5	(001)	43.4	11.7
III12-A16	46.1	(001)	46.5	7.5
III16-A12	46.6	(001)	46.7	3.8
III16-A16	49.5	(001)	49.7	5.1
III12-B12	51.9	(001)	52.1	5.9
III12-B16	55.4	(001)	55.6	4.9
III16-B12	54.6	(001)	55.5	10.3
III16-B16	59.2	(001)	59.8	8.2
IV12-A12	42.2	(001)	54.5	39.2
IV12-A16	47.6	(001)	58.3	35.2
IV16-A12	46.3	(001)	58.2	37.2
IV16-A16	50.6	(001)	61.8	35.0