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Synthesis and Mesomorphic Properties of 4,4′-Di(*n*-Alkyl)Stilbenes

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A new synthetic method to obtain only trans-isomers of 4,4′-di(*n*-alkyl)stilbenes is reported. It was found that these series of alkyl-substituted stilbenes exhibit two and three mesophases for $n = 8$, 9 and 10 and $n = 11$ and 12 respectively. The identification of the liquid crystalline phases has been carried out by miscibility tests, microscopic observations and X-ray measurements. The present study shows that all mesophases are characterized by a monolayer structure with either a pseudohexagonal (S_G) or a herringbone (S_H) arrangement of the molecular planes.

Keywords: liquid crystal, stilbene, smectic G phase, smectic H phase

1. INTRODUCTION

Numerous organic molecules exhibit smectic liquid crystalline phases and, among others, stilbene derivatives. It was recently shown that these compounds may have interesting properties depending on the nature of the conjugated systems. For example, the mesogenic stilbenes substituted by a donor at one side and an acceptor group at the opposite one are potential candidates for nonlinear optical applications.[1]

It is well established that the linear isomers of the long-chain-substituted stilbenes exhibit liquid crystalline phases, whereas the bent cis-isomers do not.[2] To date, two types (type 1 and 2) of the long-chain-substituted trans-stilbenes have been reported (Figure 1).[3–8] Conventionally these stilbenes were prepared by using the Wittig reaction,[4,5] but this method is time-consuming. Recently a new synthetic method for preparing 4,4′-di(*n-alkoxy*)stilbene (type 1) in a more rapid way was reported.[8] However, the obtained stilbenes were mainly cis-isomers (99% in relative yield). In the present work, we prepared a novel series of 4,4′-di(*n-alkyl*)stilbene

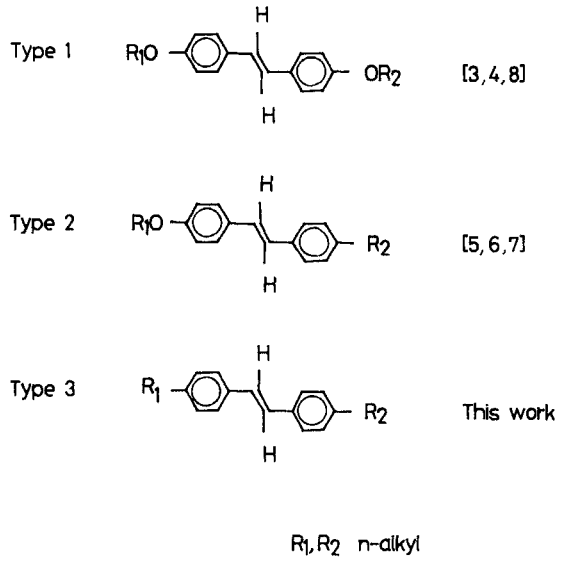

FIGURE 1 Chemical formulae.

(type 3) by the new method. It is worth mentioning that only trans-isomers of the alkyl-substituted stilbenes (noted hereafter as C_n-stilbenes) could be obtained by this synthetic method, exhibiting two mesophases for $n = 8-10$ and three mesophases for $n = 11, 12$.

The study of these mesophases was carried out by using microscopic observations, miscibility tests and differential scanning calorimetry and X-ray diffraction measurements.

2. SYNTHESIS

The synthesis of the present 4,4′-di(*n*-alkyl)stilbenes was carried out using the new method of preparation of 4,4′-di(*n*-alkoxy)stilbenes reported previously.[8] The starting material was *p*-*n*-alkylbromobenzene prepared by a modified version of the method reported by Cuellar and Marks.[9] In Table I are listed the yields and the elemental analysis data for the C_n-stilbenes from *n*-octyl (C_8) to *n*-dodecyl (C_{12}). All the C_n-stilbenes were synthesized in the same manner (Figure 2) and the detailed procedure is presented here for th C_8-stilbene:

Dry tetrahydrofuran (THF) (20 ml) was poured on magnesium (1.79 g, 74 mmol) in a flask in a nitrogen atmosphere. A small portion of a mixture of *p*-*n*-octylbromobenzene (18 g, 67 mmol: b.p. = 114°C at 0.61 mmHg) and 20 ml of THF was run in and the mixture was refluxed gently until the reaction started. Once the reaction started, the rest of the mixture was added dropwise with stirring. The addition being completed, refluxing was kept up for 12 hours. Then, the flask was cooled by immersion in ice-water. To the reaction mixture were added dropwise a catalytic amount of dichloro(1,2-bis(diphenyl-phosphino)ethane)nickel (II),

TABLE I

Yields and elemental analysis for the C_n-stilbenes compounds

n	Yields	Elemental analysis Found (calcd.)% H	C
8	31	88.96(89.04)	10.80(10.96)
9	17	88.73(88.82)	11.15(11.18)
10	22	88.41(88.63)	11.43(11.38)
11	27	88.48(88.45)	11.39(11.55)
12	26	88.41(88.30)	11.68(11.70)

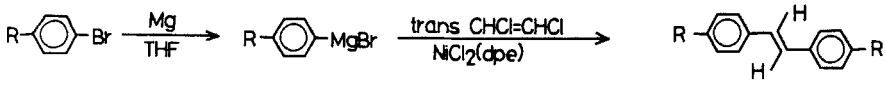

FIGURE 2 Synthetic scheme for the C_n-stilbenes.

($NiCl_2$(dpe)) (0.11 g, 0.20 mmol) and then trans-dichloro-ethylene (3.25 g, 33.5 mmol); stirring was kept up for 10 min after the end of the addition. To complete the reaction, it was refluxed for 20 hours. After the reaction mixture was cooled to room temperature, a dilute aqueous solution of hydrochloric acid was added. The mixture was immersed in an ice water bath, and the resulting solid was filtered to afford only trans-4,4′-di(*n*-octyl)stilbene. The recrystallization from acetone gave white needle-like crystals of the trans-stilbene in 31% yield. The filtrate was evaporated to give almost nothing although the yield was fairly low.

IR (KBr pellet, cm^{-1}): 2925, 2815, 1620, 1460, 960 and 820 ^{1}H-NMR ($CDCl_3$, TMS): 0.88 (*t*, J = 5 Hz, CH_3, 6H); 1.10–1.83 (*m*, CH_2, 14H); 2.56 (*t*, J = 6.6 Hz, vinylic, 2H); 7.15 (*d*, J = 9.0 Hz, aromatic, 4H); 7.29 (*d*, J = 8.4 Hz, aromatic, 4H).

3. MEASUREMENTS

The thermal analysis and the construction of miscibility diagrams were performed using a Rigaku Thermoflex TG-DSC differential scanning calorimeter (DSC). We observed the phase transition behaviours and mesomorphic textures with an Olympus BH-2 microscope with crossed polarizers and equipped with a heating plate controlled by a thermoregulator (Mettler FP80 and FP82).

X-ray diffraction powder measurements were performed with Cu-Kα radiation, using a Rigaku Geigerflex diffractometer equipped with a hand-made heating plate controlled by a thermoregulator.

The infrared spectra were recorded on a JASCO A-100 infrared spectrometer.

4. RESULTS AND DISCUSSION

4.1 Transition Temperatures

The phase transition temperatures and enthalpy changes of the present C_n-stilbene compounds are summarized in Table II. Several mesophases could be observed for each C_n-stilbene. The enthalpy changes corresponding to mesophase-mesophase transitions are significantly lower than the crystal-mesophase and mesophase-isotropic liquid ones. The transition temperatures are plotted against the number of carbon atoms in the alkyl chain in Figure 3. We have also indicated in this figure the temperatures at which the X-ray measurements were performed.

4.2 Microscopic Observation of the Mesomorphic Textures

The phase transition temperatures were also confirmed by microscopic observation. Figure 4(a) shows the texture of the high temperature mesophase (S_2) of the C_{10}-

TABLE II

Phase transition temperatures (Tt) and enthalpy changes (ΔHt) of the C_n-stilbene compounds

n	Phase $\xrightarrow[\Delta Ht(kcal/mol)]{Tt(°C)}$ Phase*
8	$K \underset{8.1}{\overset{46}{\rightleftharpoons}} S_1 \underset{0.8}{\overset{106}{\rightleftharpoons}} S_2 \underset{3.9}{\overset{108}{\rightleftharpoons}} I.L.$
9	$K \underset{9.2}{\overset{41}{\rightleftharpoons}} S_1 \underset{0.4}{\overset{93}{\rightleftharpoons}} S_2 \underset{4.2}{\overset{109}{\rightleftharpoons}} I.L.$
10	$K \underset{10.1}{\overset{64}{\rightleftharpoons}} S_1 \underset{0.4}{\overset{92}{\rightleftharpoons}} S_2 \underset{5.4}{\overset{106}{\rightleftharpoons}} I.L.$
11	$K_1 \underset{1.1}{\overset{57}{\rightleftharpoons}} K_2 \underset{4.8}{\overset{61}{\rightleftharpoons}} S_x \underset{1.7}{\overset{70}{\rightleftharpoons}} S_1 \underset{0.3}{\overset{85}{\rightleftharpoons}} S_2 \underset{5.6}{\overset{106}{\rightleftharpoons}} I.L.$
12	$K \underset{8.1}{\overset{75}{\rightleftharpoons}} S_x \underset{2.4}{\overset{77}{\rightleftharpoons}} S_1 \underset{0.2}{\overset{81}{\rightleftharpoons}} S_2 \underset{6.1}{\overset{103}{\rightleftharpoons}} I.L.$

* Phase nomenclature: K = crystal, S = smectic liquid crystal and I.L. = isotropic liquid.

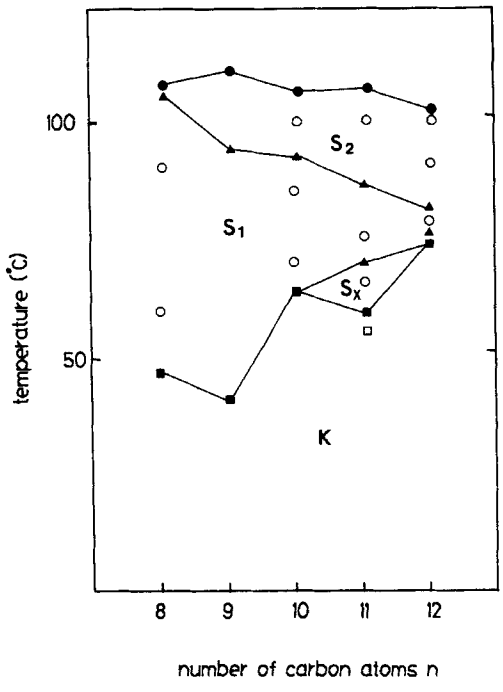

FIGURE 3 Phase transition temperatures as a function of number of carbon atoms in the alkyl chain for the C_n-stilbenes. ●, clearing point; ▲, smectic-smectic transition; ■, melting point; □, solid-solid transition; ○, X-ray measurements and microscopic observation temperatures.

stilbene at 100°C obtained by cooling the isotropic liquid. This mesophase exhibits a natural mosaic texture and the platelet areas are of an almost rectangular shape. We can also observe, in a few regions, a "Grand-jean terraces" structure which is typical of the lamellar structure of the smectic polymorphism.

On further cooling the sample, the mosaic texture remained but around the transition temperature (92°C), the mosaic areas became lined and granulated (Figure 4(b)). In addition, some areas presented a "zig-zag lines" structure in this low temperature mesophase (S_1) as can be seen in Figure 4(c). At the same time, the mosaic area borders became crinkled. According to Gray and Goodby,[10] this behaviour is good evidence of the formation of a smectic H phase. The observation is compatible with the X-ray diffraction and miscibility results to be presented and discussed below. The S_1 and S_2 mesophases of all the C_n-stilbene compounds studied in this work exhibit the same mosaic texture and lined mosaic texture as those of C_{10}-stilbene, respectively.

4.3 Miscibility Tests

These experiments were performed in a first step with standard material and the C_{10}-stilbene and then with the C_{10}- and C_{12}-stilbenes. The standard compound used in this study was the 4-nonyloxy-benzylidene-4′-butylaniline which is well known to exhibit a thermally stable smectic G phase.[11] This compound is very similar to that proposed by Gray and Goodby for miscibility tests.[10] The obtained diagrams

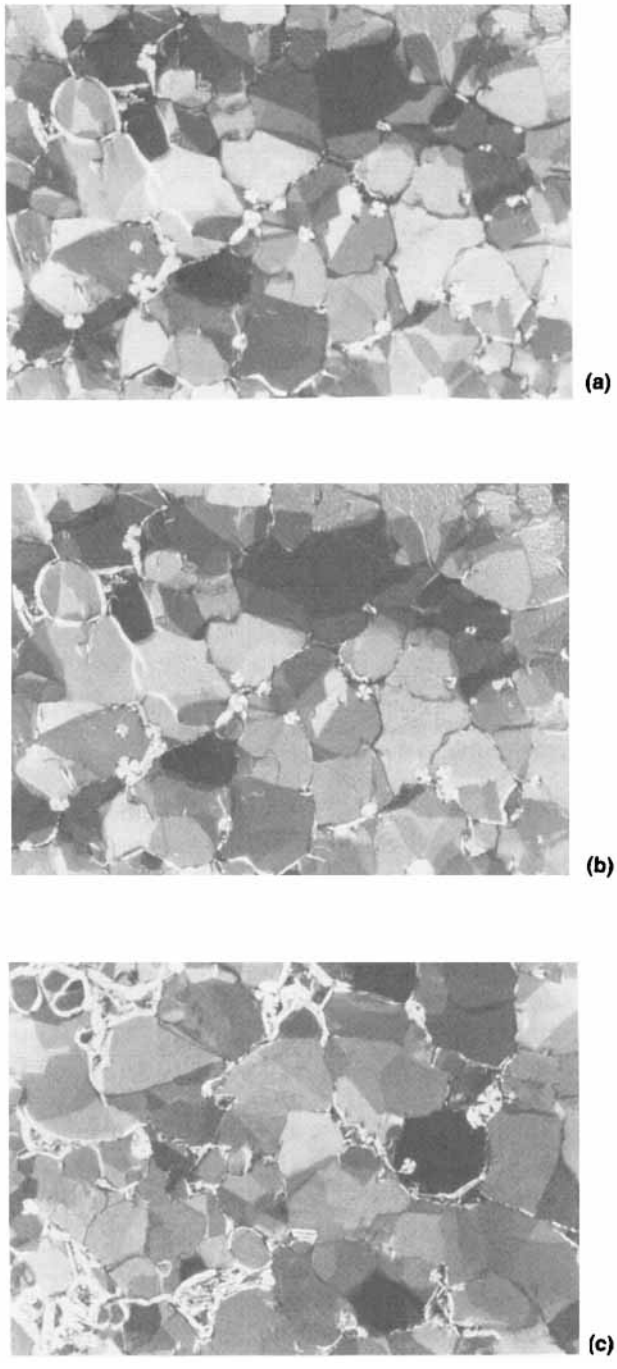

FIGURE 4 (a) The natural mosaic texture of the smectic G phase of the C_{10}-stilbene at 100°C formed on cooling the isotropic liquid. (b) The mosaic texture of the smectic H phase of the C_{10}-stilbene at 85°C. The mosaic areas became lined and granulated with crinkled area borders. (c) The same phase as (b) with the same texture but this other region presents further zig-zag lines. See Color Plate I.

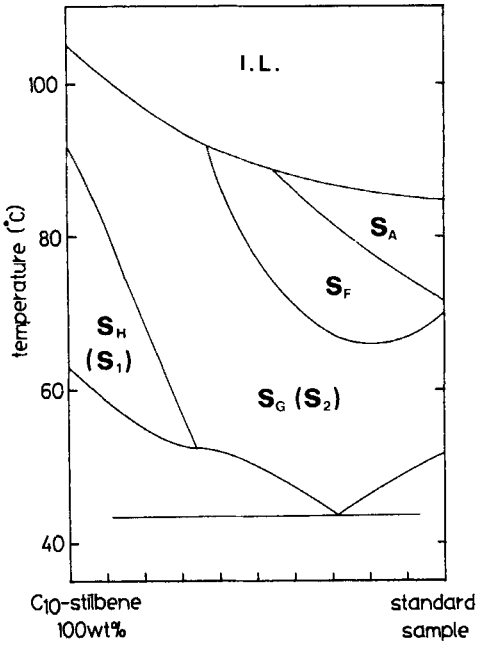

FIGURE 5 Miscibility diagram for C_{10}-stilbene and standard sample. Eutectic point: 42°C for 73 wt% of C_{10}-stilbene.

are shown in Figures 5 and 6. From Figure 5 we can deduce that the high temperature mesophase (S_2) in the present C_{10}-stilbene compound is miscible to the smectic G phase of the standard sample and consequently conclude that the S_2 mesophase is a smectic G phase (tilted S_B) which is in agreement with the exhibition of the natural mosaic texture. The second miscibility diagram (Figure 6) indicates that the S_1 and S_2 mesophases in C_{12}-stilbene are totally miscible to those of C_{10}-stilbene.

4.4 X-ray Diffraction Results

X-ray diffraction (XRD) measurements of powder samples were performed for all C_n-stilbenes in the crystalline state and in the mesophases. Figure 7 shows the diffraction spectra of the C_{10}-stilbene obtained on cooling the isotropic liquid: (a) in the high temperature mesophase (S_2), (b) and (c) in the low temperature one (S_1) and (d) in the crystalline phase (K).

Similar XRD spectra have been obtained with the other compounds except for the C_{11}- and C_{12}-stilbenes which exhibit one additional mesophase (S_x) below the S_1 mesophase. The XRD spectrum of the S_x mesophase is given in Figure 8 for C_{11}-stilbene.

The crystalline (K) phase in Figure 7(d) can be characterized by a large number of sharp reflections spread all over the angle region scanned ($2° < 2\theta < 60°$). The XRD spectra in Figure 7(a–c) for the mesophases show one or more sharp reflections superimposed on a very broad reflection which appears in the Bragg angle

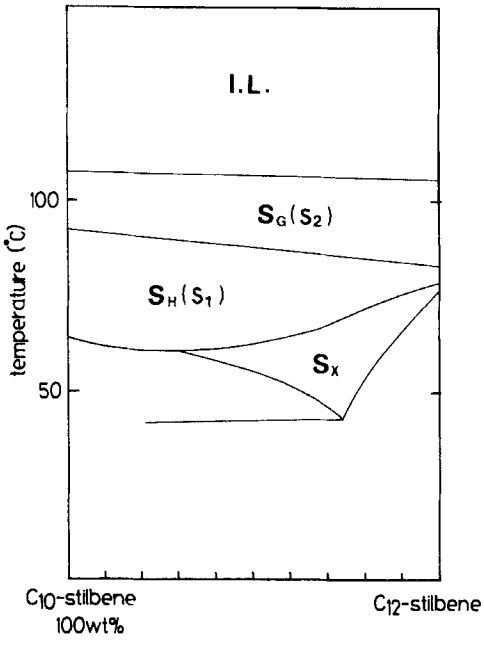

FIGURE 6 Miscibility diagram for C_{10}-stilbene and C_{12}-stilbene. Eutectic point: 44°C for 71 wt% of C_{10}-stilbene.

region between 16° and 24°. In the low Bragg angle region, strong and sharp reflections appear in all cases and their corresponding spacings are exactly in the ratios: 1:1/2:1/3:1/4. This is a characteristic of the lamellar structure of smectic mesophases and corresponds to the reticular spacing (001), (002), (003) and (004).

As illustrated in Figure 9, the interlayer distances d_{001} remain almost constant throughout the entire mesophase temperature range. A similar behaviour was obtained in the X-ray studies with TBPA and TBBA compounds which exhibit a smectic G- smectic H transition.[12] The high temperature mesophase (S_2) in the present C_{10}-stilbene was identified by the miscibility test as a smectic G phase as described above. The smectic H phase is usually obtained by cooling the smectic G phase.[13] As mentioned above, the zig-zag-lined mosaic texture suggests strongly that the lower temperature mesophase (S_1) is a smectic H phase. These arguments are well supported by the constant value of the interlayer distance d_{001}.

In this context, the XRD spectra were analyzed on the basis of monoclinic three-dimensional lattices. Our XRD data analysis was based on the consideration of Doucet *et al.*[12] in their study of the TBBA compound: the strongest reflections are attributed to the (110) and (200) reticular reflections. Using these assumptions, we indexed all lines and calculated the unit cell parameters. These values are reported in Table III. In the case of the smectic G (S_2) phase, where only the (110) reflection appears, the tilted angle was calculated from the interlayer distance d_{001} and by assuming that the *c*-axis parameter has the same value as in the smectic H (S_2) phase. These results are in agreement with the ones obtained in the case of the TBBA compound which exhibits the same transition and the proposed structure

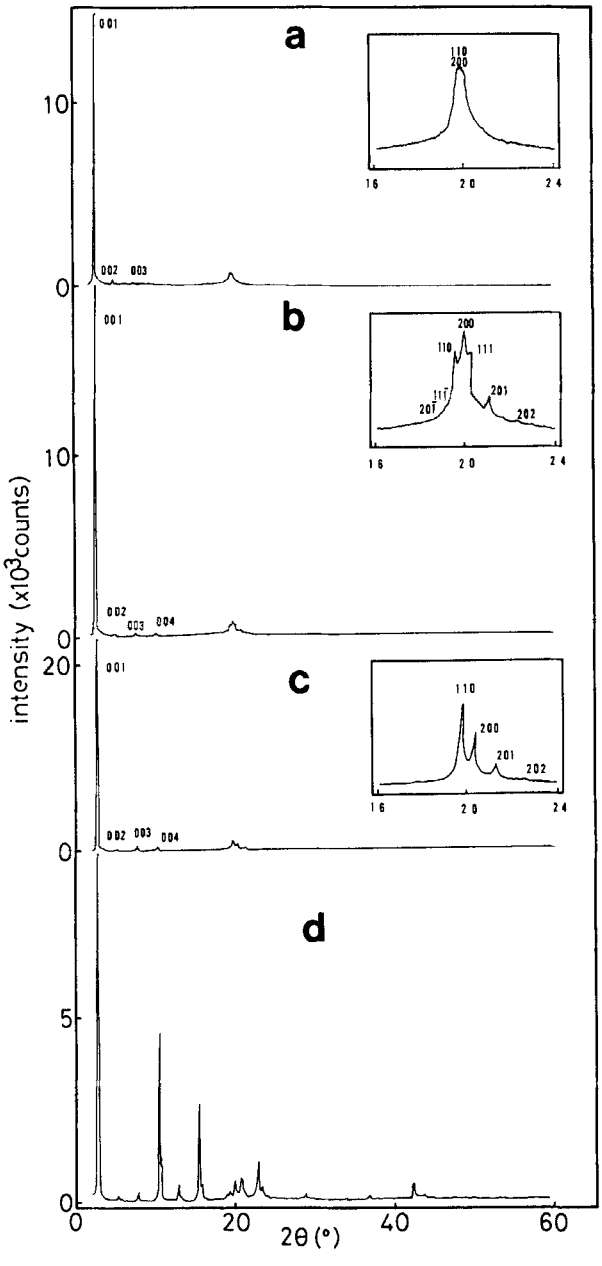

FIGURE 7 X-ray diffraction powder spectra obtained on cooling the isotropic liquid. In the insets, the 16°–24° Bragg angle of each spectrum is given in detail: (a): the S_2 mesophase (smectic G phase) at 100°C; (b): the S_1 mesophase (smectic H phase) at 85°C; (c): the S_1 mesophase (smectic H phase) at 70°C; and (d): the crystalline phase (K) at room temperature.

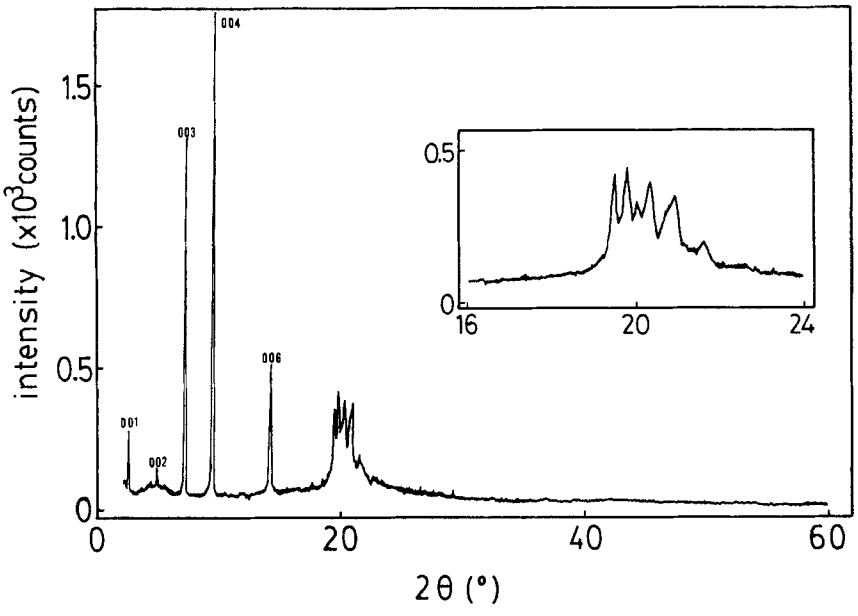

FIGURE 8 X-ray diffraction spectrum of the S_x mesophase for the C_{11}-stilbene formed on cooling the smectic H phase. In the inset, the 16°–24° region is given in detail.

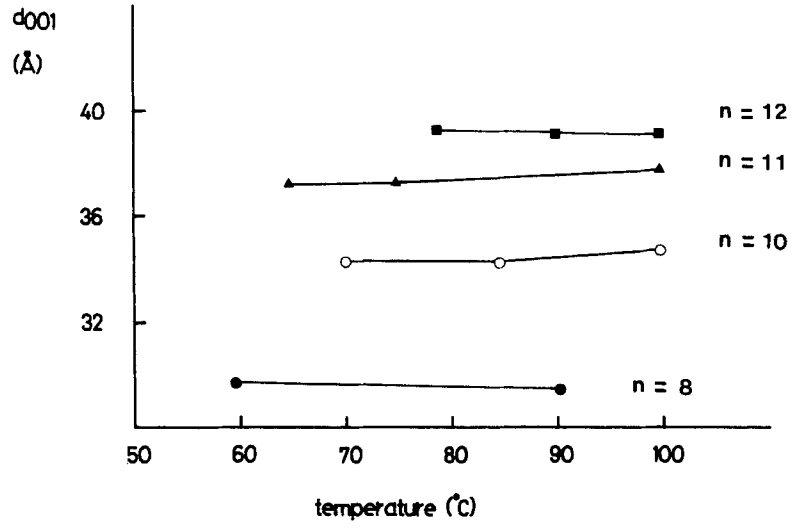

FIGURE 9 The interlayer distance d_{001} in the smectic phases as a function of temperature for C_n-stilbenes.

in the layer. In the case of the smectic G phase, the molecules can rotate freely around the molecular axis which makes all the sites equivalent, leading to a two-dimensional pseudohexagonal arrangement in the plane perpendicular to the smectic layer. In the smectic H phase which is obtained by cooling the smectic G phase, the molecules are arranged in a herringbone-type structure and can only oscillate

TABLE III

X-ray diffraction data for S_2 (smectic G), S_1 (smectic H) and S_x mesophases in the C_n-stilbene compounds

n = 8

S_1 (S_H) at 90°C			S_1 (S_H) at 60°C		
$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	d_{calc} (Å)	(hkl)
28.97	28.97	(001)	29.17	29.17	(001)
14.48	14.48	(002)	14.87	14.59	(002)
9.66	9.52	(003)	9.92	9.72	(003)
7.27	7.24	(004)	7.42	7.29	(004)
4.86	4.86	(20$\bar{2}$)			
4.70	4.69	(11$\bar{1}$)	4.58	4.58	(11$\bar{1}$)
4.59	4.59	(110)	4.51	4.51	(110)
4.47	4.47	(200)	4.34	4.35	(200)
4.40	4.40	(111)			
4.14	4.18	(201)	4.10	4.10	(201)
a= 9.8 Å			a= 9.3 Å		
b= 5.4 Å			b= 5.3 Å		
c= 32.1 Å			c= 31.8 Å		
β= 114°			β= 111°		

* The S_2 mesophase could not be characterized by the X-ray study because the mesomorphic range is too narrow to measure.

n = 10

S_2 (S_G) at 100°C			S_1 (S_H) at 85°C			S_1 (S_H) at 70°C		
$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)
33.36	33.36	(001)	34.11	34.11	(001)	33.36	33.36	(001)
17.33	16.68	(002)	17.09	17.06	(002)	17.08	16.68	(002)
11.57	11.12	(003)	11.41	11.37	(003)	11.40	11.12	(003)
			8.55	8.53	(004)	8.58	8.34	(004)
			4.65	4.63	(20$\bar{1}$)			
			4.61	4.62	(11$\bar{1}$)			
		(110)	4.55	4.55	(110)	4.50	4.50	(110)
4.50	4.50							
		(200)	4.46	4.46	(200)	4.37	4.37	(200)
			4.42	4.42	(111)			
			4.24	4.25	(201)	4.18	4.18	(201)
			3.98	4.00	(202)	3.88	3.95	(202)
a= 9.1 Å			a= 9.4 Å			a= 9.2 Å		
b= 5.2 Å			b= 5.3 Å			b= 5.2 Å		
c= 36.2 Å			c= 36.2 Å			c= 36.0 Å		
β= 108°			β= 109°			β= 108°		

around their equilibrium position leading to a rectangular arrangement in the plane perpendicular to the smectic layer. Hence this phase presents a higher local order than the preceeding smectic G one.

If we assume that the long molecular axis is parallel to the *c*-axis in the present smectogens, we find that the *c* parameter is smaller than the fully extended mo-

TABLE III (*continued*)

n = 11

S_2 (S_G) at 100°C			S_1 (S_H) at 75°C			S_x at 65°C		
$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)
37.16	37.16	(001)	36.32	36.32	(001)	36.56	36.56	(001)
18.84	18.58	(002)				18.63	18.28	(002)
12.57	12.37	(003)	12.39	12.11	(003)	12.40	12.19	(003)
						9.29	9.14	(004)
						6.19	6.09	(006)
			4.53	4.50	(11$\bar{1}$)	4.56	-	-
		(110)	4.45	4.45	(110)	4.49	-	-
4.49	4.49					4.43	-	-
		(200)	4.38	4.38	(200)	4.37	-	-
			4.33	4.33	(111)	4.28	-	-
			4.20	4.20	(201)	4.25	-	-
			3.99	3.98	(202)	4.12	-	-
a= 9.0 Å			a= 9.2 Å					
b= 5.2 Å			b= 5.2 Å					
c= 39.2 Å			c= 39.2 Å					
β= 106°			β= 108°					

n = 12

S_2 (S_G) at 100°C			S_2 (S_G) at 90°C			S_1 (S_H) at 79°C		
$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	(hkl)
36.70	36.70	(001)	38.53	38.53	(001)	38.21	38.21	(001)
19.45	18.35	(002)	19.42	19.27	(002)	19.63	19.11	(002)
13.07	12.23	(003)	13.08	12.84	(003)	13.06	12.74	(003)
						9.83	9.55	(004)
		(110)			(110)	4.48	4.48	(110)
4.46	4.46		4.46	4.46				
		(200)			(200)	4.42	4.42	(200)
						4.25	4.25	(201)
						4.05	4.05	(202)
			a= 9.0 Å			a= 9.2 Å		
			b= 5.2 Å			b= 5.2 Å		
			c= 40.9 Å			c= 40.9 Å		
			β= 107°			β= 106°		

lecular length calculated from the C.P.K. model: 34.6ÅP : 40.8ÅP : 43.9ÅP and 46.9ÅP for n = 8 : 10 : 11 and 12 respectively. Hence, we can conclude that both smectic phases (S_1) and (S_2) have a monolayer structure with a shrinkage of the terminal alkyl chains of about: 7% : 11% : 12% and 13% for n = 8 : 10 : 11 and 12 respectively.

It should be noted that the XRD pattern (see Figure 8) corresponding to the additional mesophase (S_x) in the C_{11}-stilbene seems difficult to analyze. Five sharp reflections were observed at the low Bragg angle region and their spacings are exactly in the ratios: 1 : 1/2 : 1/3 : 1/4 : 1/6 which permit us to deduce that the mesomorphic structure is lamellar. Hence, this mesophase (S_x) exhibits a monolayer lamellar structure and the value of the periodicity between the layers is 37.2ÅP. Besides these reflections, a diffuse element appears around 2θ = 20° with several

sharp peaks. Apparently, this mesophase possesses a higher local order within the layers than the preceeding S_G and S_H ones. This phase should not be crystalline but mesomorphic because of the abscence of reflections outside the angle region of the broad one. Furthermore its microscopic texture remains mosaic before the sudden crystallization at 57.8°C in the cooling stage (Figure 10). The identification of this rigid lamellar mesophase probably requires X-ray diffraction study on single domains.

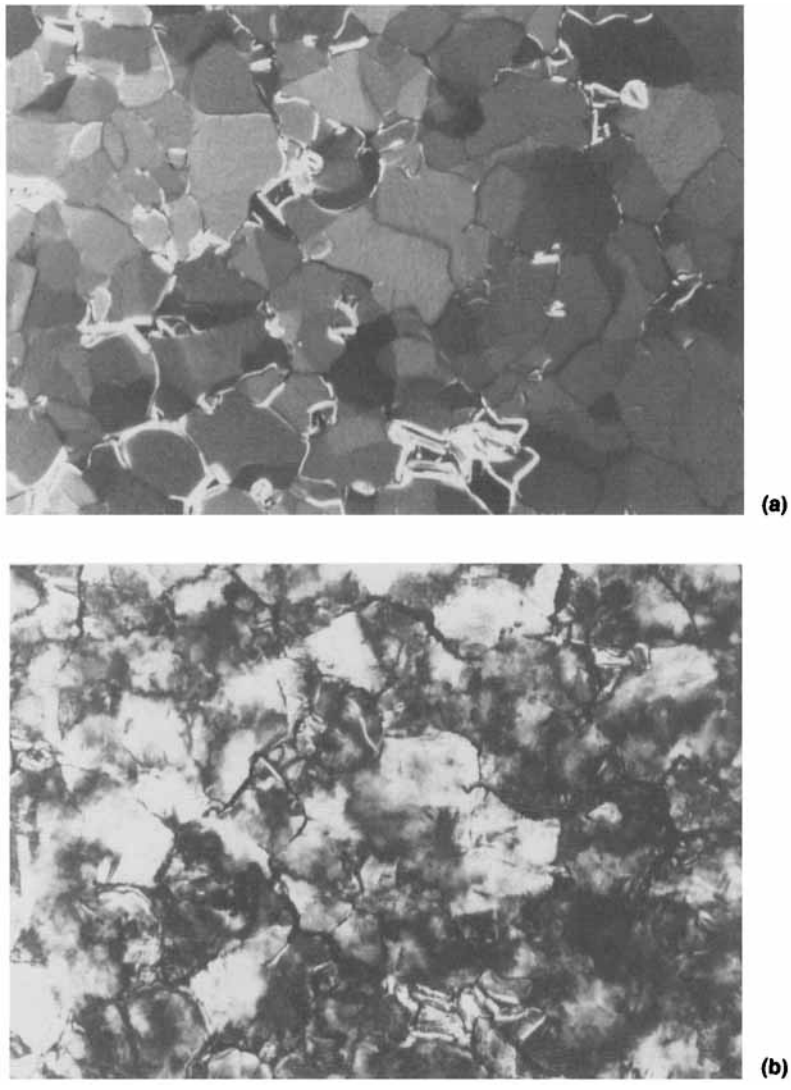

FIGURE 10 (a) The mosaic texture of the unidentified S_x phase of the C_{11}-stilbene at 59°C formed on cooling the smectic H. (b) The solid phase texture of the C_{11}-stilbene obtained on cooling the mosaic texture of the unidentified S_x phase. See Color Plate II.

5. CONCLUSION

In this work, we have used a recently reported synthetic method leading solely to trans-isomers of di(*n*-alkyl)stilbenes. The DSC study, the miscibility tests, the microscopic observations and the X-ray measurements characterized the obtained compounds. All mesophases possess a monolayer structure. It was found that all compounds exhibit a smectic G-smectic H transition. For $n = 11$ and 12, a third smectic phase can be observed by cooling the smectic H phase. This phase presents a higher local order than the preceeding one but the same microscopic texture.

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