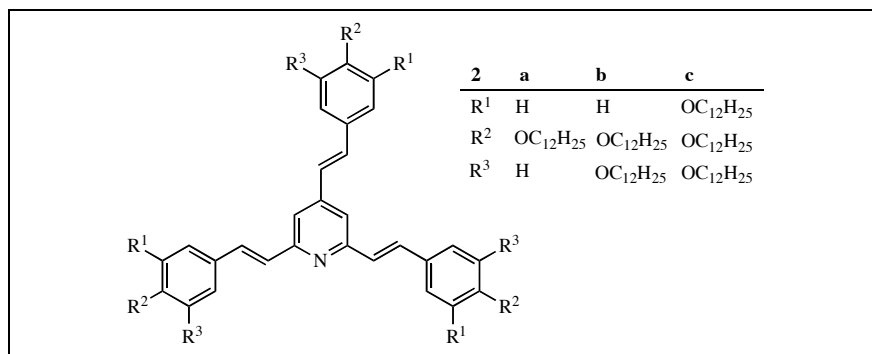


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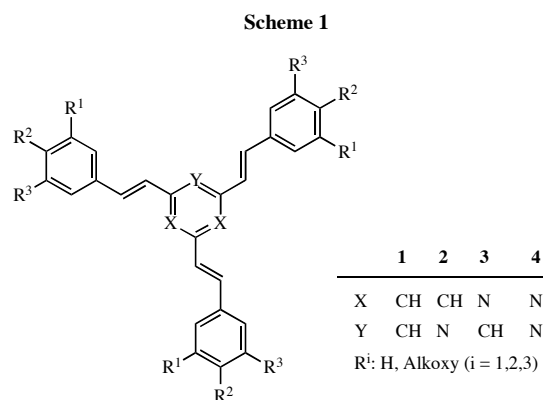


(*E,E,E*)-2,4,6-Tris(styryl)pyridines **2a-c** with 3, 6 or 9 dodecyloxy substituents were prepared by the highly stereoselective condensation reaction of collidine (**8**) and the corresponding phenyl-(1-phenylmethylidene)amines **7a-c** (Siegrist reaction). In contrast to the corresponding compounds with a benzene or a 1,3,5-triazine core, **2a-c** do not show any hints for the formation of thermotropic liquid crystals. The major application of such star-shaped systems is in the field of nonlinear optics.

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Conjugated star-shaped compounds have interesting electrical, optical and optoelectronic properties, which permit various applications in materials science (nonlinear optics NLO, field effect transistors FET, light emitting diodes LED, *etc.*) [1]. This structure unit can also serve as mesogen for the formation of liquid crystals [LC] {discotic nematic (N_D), columnar nematic (N_C) or columnar (Col_h, Col_{ob}, Col_r, *etc.*) thermotropic phases} [2]. Scheme 1 shows 1,3,5-tris(styryl)benzenes **1** and the corresponding pyridines **2**, pyrimidines **3** and 1,3,5-triazines **4**.

Although the parent systems (R = H) have been known for a long time (**1** [3], **2** [4], **3** [5], **4** [6]), only very few derivatives with long flexible side chains R have been prepared. Such side chains are a precondition for the formation of LC phases. (*E,E,E*)-1,3,5-Tris(styryl)-benzenes **1** with nine OC₆H₁₃ or OC₁₂H₂₅ groups (R¹ = R² = R³) form Col_h phases [7-9]. (*E,E,E*)-2,4,6-Tris(styryl)pyridine **2** with six decyloxy groups (R¹ = H, R² =



R³ = OC₁₀H₂₁) and two additional CN groups on the pyridine ring forms a Col_h phase as well [10]. Until now – to our best knowledge – pyrimidines **3** with side chains were not studied. Most examples of LC phases exist in the series of 1,3,5-triazines **4** with six octyloxy chains (R¹ =

Table 1

¹H NMR data of **2a-c** (δ values in CDCl₃, TMS as internal standard).

Comp.	Pyridine	2-Styryl, 6-Styryl		4-Styryl		OC ₁₂ H ₂₅	CH ₂	CH ₃
	3-H, 5-H	olefin. H [a]	aromat. H	olefin. H [a]	aromat. H	OCH ₂	CH ₂	CH ₃
2a	7.24 (2H)	7.07 (2H)	6.90 (4H)	6.89 (1H)	6.89 (2H)	4.00 (6H)	1.20-1.85 (60H)	0.89 (9H)
2b	7.31 (2H)	7.07 (2H)	7.53 (4H)	7.28 (1H)	7.47 (2H)	4.05 (12H)	1.20-1.88 (120H)	0.89 (18H)
2c	7.36 (2H)	7.10 (2H)	7.11 (2H)	7.27 (1H)	7.06 (1H)	4.03 (18H)	1.20-1.85 (180H)	0.89 (27H)
		7.56 (2H)	7.18 (2H)	7.09 (1H)	7.09 (1H)			
			6.81 (4H)	6.91 (1H)	6.76 (2H)			
			7.24 (1H)	7.24 (1H)				

[a] ³J = 16.1 ± 0.1 Hz

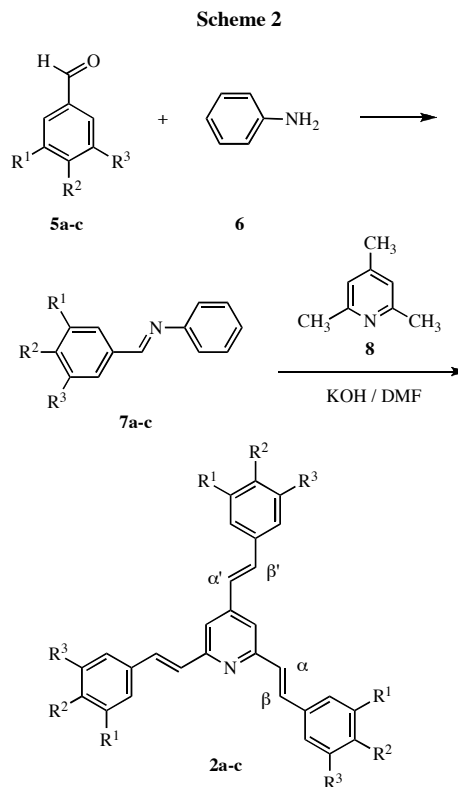
H, $R^2 = R^3 = \text{OC}_8\text{H}_{17}$) or nine OC_6H_{13} , OC_8H_{17} , $\text{OC}_{10}\text{H}_{21}$, $\text{OC}_{12}\text{H}_{25}$, $\text{OC}_{16}\text{H}_{33}$ or $\text{O}(\text{CH}_2)_2\text{-CH}(\text{CH}_3)\text{-(CH}_2)_3\text{-CH}(\text{CH}_3)_2$ chains [11-13]. We studied now pyridines **2** with 3, 6, and 9 $\text{OC}_{12}\text{H}_{25}$ groups.

The synthetic approach (Scheme 2) started with the formation of the corresponding aldimines **7a-c** from the aldehydes **5a-c** and aniline **6**: **7a** [14], **7b** [15], **7c** [15,16]. Commercially available 2,4,6-trimethylpyridine (collidine) **8** was then reacted with **7a-c**. The first two condensation processes in 2- and 4-position are fast. The third condensation step (in 6-position) is much slower as ^1H nmr reaction spectra revealed. The yield of the Siegrist reaction [17] $\mathbf{7} + \mathbf{8} \rightarrow \mathbf{2}$ is generally lower than that of comparable processes as for example the Knoevenagel condensation or the Wittig-Horner reaction, but the stereoselectivity in favor of the (*E*)-configurations is extremely high. The kinetically controlled Siegrist reaction [18] leads to *Z/E* ratios which are below 1:99, which means below the thermodynamic equilibrium, which is in the case of 1,2-di(het)arylethenes in the range of 5:95.

The ^1H nmr characterization of the target compounds **2a-c** is summarized in Table 1. Typical is the splitting $\Delta\delta$ of the olefinic AB spin systems with coupling constants of 16 ± 0.1 Hz. It indicates the polarization of the olefinic double bonds which is for **2** higher than for the benzene derivatives **1**, but lower than for the corresponding 1,3,5-triazines **4** [12,14]. According to the push-pull effect, the resonance of the α and α' protons in **2a-c** (Scheme 2, Table 1) is always at higher field than the resonance of the β and β' protons. Table 2 shows the ^{13}C nmr data of **2a-c**. The polarization of the olefinic CC bonds is demonstrated by $\Delta\delta$ values between 4.9 and 8.5 ppm.

Thermotropic liquid crystalline phases could not be detected by DSC for **2a-c**. Compound **2c** would fulfill the best prerequisites for a columnar aggregation because the disc, formed by sp^2 carbon atoms, has a diameter of about 190 pm [10] (suitable for the π stacking) and nine dodecyloxy chains should provide sufficient Van der Waals interactions. In contrast to the crystalline states of

2a and **2b** at ambient temperatures with sharp melting points at 43 and 69 °C, respectively, **2c** is a viscous oil, which solidifies below 0 °C to a glass [19].



2	a	b	c
R^1	H	H	$\text{OC}_{12}\text{H}_{25}$
R^2	$\text{OC}_{12}\text{H}_{25}$	$\text{OC}_{12}\text{H}_{25}$	$\text{OC}_{12}\text{H}_{25}$
R^3	H	$\text{OC}_{12}\text{H}_{25}$	$\text{OC}_{12}\text{H}_{25}$
mp [°C]	43	69	< 0
Yield [%]	66	45	19

Star-shaped compounds with polar end groups as **2a-c** have high hyperpolarizabilities. Therefore nonlinear optics are the preferred area of application in materials science [2].

Table 2

^{13}C NMR data of **2a-c** (δ values in CDCl_3 , TMS as internal standard).

Comp.	Pyridine Ring			Vinylene Bridges				Benzene Rings [a]			$\text{OC}_{12}\text{H}_{25}$ Chains [a]			
	C-2,6	HC-3,5	C-4	$\alpha\text{-CH}_2$	$\beta\text{-CH}_2$	$\alpha'\text{-CH}_2$	$\beta'\text{-CH}_2$	CH	C_q	C_qO	OCH ₂	CH ₂	CH ₃	
2a	155.9	117.0	145.7	126.2	132.2	123.9	132.0	114.6	129.0	159.3	67.9	22.7	29.4	14.1
								114.7				26.0	29.6	
								128.3				29.2	31.9	
								128.4				29.3		
2b	156.0	117.7	145.7	126.4	132.6	124.1	132.6	111.6	129.3	149.1	69.1	22.7	29.4	14.1
								113.3	129.8	149.2	69.3	26.0	29.6	
										149.5		29.3	31.9	
										149.9				
2c	156.0	116.4	145.6	128.1	133.0	126.1	133.0	105.7	131.5	138.3	69.1	22.7	29.7	14.1
									131.9	139.3	73.5	26.1	31.9	
										153.3		29.4		
										153.4				

[a] Partly overlapping signals

EXPERIMENTAL

The melting points were determined on a Büchi melting point apparatus and are uncorrected. Their control was performed with a Perkin-Elmer DSC-7. The ^1H and ^{13}C nmr data were obtained on Bruker AM 400 and AC 200 spectrometers using CDCl_3 as solvent and TMS as internal standard. The FD mass spectra were recorded on a Finnigan M95 spectrometer. A Beckman Acculab spectrometer served for the measurements of the ir spectra in KBr or as neat films. The elemental analyses were performed in the microanalytical department of the institute.

General Procedure for the Preparation of the (E,E,E)-2,4,6-Tris(styryl)pyridines 2a-c. A slow oxygen-free stream of N_2 was purged for 30 min through a solution of 2,4,6-trimethylpyridine (collidine) (**8**) (606 mg, 5.0 mmol) and 16.5 mmol aldimine **7a-c** [14,15] in DMF (150 mL). To the vigorously stirred solution powdered KOH (3.70 g, 66 mmol) was added and the temperature was raised to 90 °C. After 1 h the reaction mixture was cooled to 0-5 °C and CH_3OH (200 mL) was added dropwise. The products **2a** and **2b** precipitated and were washed with aqueous CH_3OH . Oily product **2c** was extracted with 2 x 100 mL $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ from the CH_3OH phase to which 200 mL H_2O was added. The dried (MgSO_4), crude products were purified by column chromatography (6 x 50 cm SiO_2 , toluene or toluene/ethyl acetate 100:2). The compounds **2a** and **2b** can be recrystallized from acetone.

(E,E,E)-2,4,6-Tris[2-(4-dodecyloxyphenyl)vinyl]pyridine (2a) Yield: 3.097 g (66%). Pale yellow crystals which melted at 43 °C; ir (KBr): 2890, 2820, 1565, 1495, 1450, 1415, 1245, 1120, 950 cm^{-1} ; FD ms: m/z (%) 938 (100) [M^+]. Anal. Calcd. for $\text{C}_{65}\text{H}_{95}\text{NO}_3$ (938.5): C, 83.19; H, 10.20; N, 1.49. Found: C, 83.12; H, 10.21; N, 1.66.

(E,E,E)-2,4,6-Tris[2-(3,4-didodecyloxyphenyl)vinyl]pyridine (2b) Yield: 3.354 g (45%). Pale yellow crystals which melted at 69 °C; ir (KBr): 2895, 2825, 1590, 1570, 1520, 1495, 1455, 1235, 1160, 960, 840 cm^{-1} ; FD ms: m/z (%) 1492 (100) [$\text{M}+\text{H}^+$]. Anal. Calcd. for $\text{C}_{101}\text{H}_{167}\text{NO}_6$ (1491.4): C, 81.34; H, 11.29; N, 0.94. Found: C, 81.35; H, 11.14; N, 1.08.

(E,E,E)-2,4,6-Tris[2-(3,4,5-tridodecyloxyphenyl)vinyl]pyridine (2c) Yield: 1.944 g (19%) [20]. Pale yellow oil; ir (neat film): 2890, 2820, 1565, 1485, 1420, 1365, 1325, 1230, 1105, 955 cm^{-1} ; FD ms: m/z (%) 2046 (100) [$\text{M}+\text{H}^+$]. Anal. Calcd. for $\text{C}_{137}\text{H}_{239}\text{NO}_9$ (2044.4): C, 80.44; H, 11.78; N, 0.69. Found: C, 80.11; H, 11.95; N, 0.82.

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- [16] The reaction can be performed without solvent when the generated water is removed by working at 2.1 kPa. The yields of the products are then almost quantitative: **7a** (95%), **7b** (97%), **7c** (98%).
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- [19] The phase transition enthalpies ΔH for **2a** and **2b** amount to 31 and 55 kJ mol^{-1} , respectively. An LC phase of **2c** within a small temperature interval above 0 °C could not be completely excluded by DSC, but such a possible phase would have no applications in materials science.
- [20] Extension of the reaction time to 6 h enhances somewhat the yield of the crude product, but makes the purification more difficult.