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# Alkoxy substituted (*E*,*E*)-3,6-bis(styryl)pyridazine—a photosensitive mesogen for liquid crystals

Thorsten Lifka, Georg Zerban, Peter Seus, Annette Oehlhof, Herbert Meier\*

Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

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### 1. Introduction

Stilbenoid compounds play an important role in materials science because their photo- and electroactive chromophores/ fluorophores have tunable properties for various applications as optical brighteners, laser dyes, scintillators, (photo)conductors, photoresists, nonlinear optical (NLO) materials, electroluminescent materials, etc.<sup>1,2</sup> Moreover, stilbenes and related systems belong to the best studied classes of compounds in organic photochemistry.<sup>2</sup> They can show *E/Z* isomerization reactions, (oxidative) cyclizations, cyclodimerizations, and crosslinking processes on irradiation.

Extension of the (E)-stilbene chromophore to (E,E)-1,4-bis(styryl)benzene (**1**) (Scheme 1) provokes not only a red-shift of absorption



**Scheme 1.** 1,4-Bis(styryl)benzenes **1** and the related azines **2–7** with 1–4 nitrogen atoms in the central ring (R=H, alkyl, alkoxy, etc.).

\* Corresponding author. Fax: +49 6131 3925396. E-mail address: hmeier@mail.uni-mainz.de (H. Meier).

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#### ABSTRACT

(*E*,*E*)-3,6-Bis(styryl)pyridazines (**3a**-**t**) bearing 2, 4 or 6 alkoxy chains were prepared by applying the Siegrist reaction of 3,6-dimethylpyridazine (**13**) and the corresponding azomethines **10a**-**t**. The transversal dipole moment of these calamitic compounds effects an extremely high tendency for self-organization in thermotropic LC phases (N, S<sub>A</sub>, S<sub>B</sub>, S<sub>C</sub>, S<sub>E</sub>, S<sub>I/F</sub>, and Cub). The conjugated core structure represents moreover a chromophore with a high photosensitivity for (*E*,*E*)  $\rightleftharpoons$  (*E*,*Z*) isomerization reactions: this property makes the compounds interesting for optical imaging and switching techniques.

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and fluorescence bands and an increase of absorption and emission intensity ( $\varepsilon_{\text{max}}$  and fluorescence quantum yield  $\phi_{\text{F}}$ ), it changes also the photochemical behavior. Compound **1** has an extremely low tendency for photoisomerization reactions ( $\phi_{E\rightarrow Z} \approx 10^{-4}$ ).<sup>2</sup>

Therefore cyclization reactions cannot be observed. Preparative  $[2\pi+2\pi]$ cyclodimerization processes are also not usual; they occur at most as by-reactions in photocrosslinkings on irradiation with energy-rich UV light.<sup>2</sup> Thus, **1** represents a rigid but relatively photostable mesogen for calamitic and phasmidic LC systems (liquid crystals).<sup>3</sup> A degradation of the mesophases is principally possible, when hard UV light (254 nm) is used. Moreover, the conjugated scaffold of **1** can be applied for photoinduced one-dimensional energy and electron transfer<sup>4,5</sup> and for third order optical nonlinearity.<sup>6</sup>

To maintain all these properties, and to guarantee additionally facile and effectively reversible optical switching processes, we slightly changed the structure concept and involved N atoms in the central ring, which should enhance the possibility of E/Z isomerizations in the triplet state. Scheme 1 depicts the bis(styryl)azines **2–7**, which contain 1–4 nitrogen atoms.

The parent system, pyridine **2** (R=H) and some simple derivatives (R=*p*-CH(CH<sub>3</sub>)<sub>2</sub>, *p*-C<sub>6</sub>H<sub>5</sub>, *o*-OCH<sub>3</sub>, *m*-OCH<sub>3</sub>, *p*-OC<sub>2</sub>H<sub>5</sub>, *p*-N(CH<sub>3</sub>)<sub>2</sub>, and *p*-COOCH<sub>3</sub>) are known.<sup>7,8</sup> Their flexible side chains are not long enough to permit mesophase formation. An analogous statement is valid for pyridazine **3**, for which the parent system (R=H) and some derivatives (R=*o*-F and *p*-F) were reported.<sup>9,10</sup> The pyrimidines **4** and the triazines **6** are—to our best knowledge—unknown. The parent pyrazine **5** (R=H) and some of its derivatives (R=*p*-CH<sub>3</sub>, *p*-C<sub>2</sub>H<sub>5</sub>, *p*-C<sub>6</sub>H<sub>5</sub>, and *p*-OCH<sub>3</sub>) can be found in the literature.<sup>11-15</sup> Until now, none of the azines **2–6** served as mesogen in liquid crystalline compounds. Some years ago, we prepared the first tetrazines of structure **7**, the parent compound (R=H) and some



derivatives (R=*p*-OH, *p*-OCOCH<sub>3</sub>, *p*-OC<sub>12</sub>H<sub>25</sub>, *m*-OC<sub>12</sub>H<sub>25</sub>, and *p*-OC<sub>12</sub>H<sub>25</sub>).<sup>16</sup> 3,6-Bis(4-dodecyloxystyryl)-1,2,4,5-tetrazine showed a broad nematic phase in the temperature range between 228.5 and 156.1 °C (DSC cooling curve). Whereas the solution photolysis of **7** led to the fragmentation of the tetrazine ring, the LC phase proved to be rather photostable. A specialty of the tetrazine ring system is the efficient internal conversion  $S_2(\pi\pi^*) \rightarrow S_1(n\pi^*)$ , which causes the loss of the typical stilbene photochemistry.

Now, we decided to use the pyridazine structure **3** as mesogen. The transversal dipole moment should enhance the tendency of self-organization and the existence of  $\pi\pi^*$  and  $n\pi^*$  states should favor the formation of triplet states by intersystem crossing (ISC) and consequently favor reversible  $E \rightleftharpoons Z$  photoisomerization reactions.

#### 2. Results and discussion

#### 2.1. Synthesis of the (E,E)-3,6-bis(styryl)pyridazines 3a-t

The synthetic approach to the target compounds **3a–t** is illustrated in Scheme 2. The corresponding aldehydes **8a–t** were transformed with aniline (**9**) to the azomethines (Schiff bases) **10a–t**. The condensation process was performed in the absence of solvents and afforded quantitative yields when the generated water was continuously removed under reduced pressure.

3,6-Dimethylpyridazine (**13**) was obtained from 2,5-hexanedione (**11**) and hydrazine. The intermediate tautomeric dihydropyridazines generated the tricyclic dimer **12**, which was dehydrogenated to **13**. $^{9,17-19}$ 

The subsequent twofold Siegrist reaction<sup>20,21</sup> **13+10a-t** led under kinetic control to highly pure (*E*,*E*) configurations of **3a-t**. Eventually present (*E*,*Z*) configurations were below 2%, the here achieved detection limit in the <sup>1</sup>H NMR spectroscopy. The yields of **3a-t** vary strongly. Apart from the different electrophilicity of the imine carbon atom, steric shielding of the reactive center, caused by long alkoxy chains, and in particular the solubility of the components seem to have a great effect. The highest yields (60–70%) were obtained for **3d**,**g**,**I**,**m** and the lowest yields (<10%) for **3b**,**c**,**e**,**i**,**j**,**o**. An increasing number of alkoxy chains enhances the solubility of **3** and **10** in many organic solvents.<sup>22</sup> The length of the chains has also a big effect on the solubility; it increases in CHCl<sub>3</sub> from OCH<sub>3</sub> to OC<sub>6</sub>H<sub>13</sub> and decreases then for longer alkoxy chains, whereby OC<sub>12</sub>H<sub>25</sub> seems to represent another solubility maximum.

The <sup>1</sup>H and <sup>13</sup>C NMR data of the target compounds **3** are listed in Tables 1 and 2. The averaged chemical shifts of the central  $\pi$ system of **3a-t** are illustrated in Figure 1. The alkoxy substituted 3,6-bis(styryl)pyridazines are conjugated donor–acceptor–donor systems (D–A–D).<sup>11</sup> This polarization is characterized by the <sup>13</sup>C shift difference  $\Delta\delta$  of the olefinic carbon atoms, which amounts to 11.3±2.3 ppm. The (*E*) configurations are proved by <sup>3</sup>*J*(H,H)= 16.2±0.2 Hz.

It can be assumed that the reaction of racemate **10i** and **13** led to a racemate (*R*,*R*)-**3i**/(*S*,*S*)-**3i** and the diastereomeric *meso* form (*R*,*S*)-**3i**. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> contains for the CH<sub>3</sub> group on the chiral center a doublet at 1.30 ppm. Application of Pirkle's reagent [(*R*)-2,2,2-trifluoro-1-(9-anthryl)ethanol] causes a splitting into two doublets of equivalent intensity for the *R* and the *S* configured substructures. A differentiation between the diastereomers is neither by this method nor with the shift reagent Eu(facam)<sub>3</sub> possible.<sup>23</sup> Since the reaction centers are far away from each other, one can expect for **3i** a statistical ratio (*R*,*R*)/(*S*,*S*)/(*R*,*S*)=1:1:2.

#### 2.2. Phase behavior of the (E,E)-3,6-bis(styryl)pyridazines 3a-t

The (*E*,*E*)-3,6-bis(styryl)pyrazine structure **3** proved to be an ideal mesogen for the formation of thermotropic liquid crystals.<sup>24</sup>



**Scheme 2.** Preparation of the 3,6-bis(styryl)pyridazines (*E*,*E*)-**3a–t**. (Dimer **12** consists of (1*R*,5*R*,6*R*)- and (15,55,6*S*)-1,4,7,9-tetramethyl-2,3,10,11-tetraazatricyclo[ $6.3.1.0^{2.7}$ ]-dodeca-3,9-diene).<sup>18</sup>

In contrast to (*E*,*E*)-1,4-bis(styryl)benzenes  $\mathbf{1}$ ,<sup>3</sup> even short alkoxy chains in *p*-position of the terminal benzene rings of **3** are sufficient for the generation of mesophases. Figure 2 shows the temperature ranges in which different phases of the *p*-substituted series **3a**-**h** with various OC<sub>n</sub>H<sub>2n+1</sub> groups exist. The mesomorphic behavior of these compounds is outstanding. The decisive difference between the rigid mesogens of **1** and **3** consists in the transversal dipole moment of the heterocycles **3**.

Compounds **3a–d** (n=1, 2, 4, 6) form nematic phases at high temperatures. The upper limit of their temperature range (T>300 °C) is determined by starting decomposition. When temperatures above 300 °C are avoided, the second heating curves in the differential scanning calorimetry (DSC) have the same maxima

Table 1 $^{1}$ H NMR data of the pyridazines **3a-t** ( $\delta$  values in CDCl<sub>3</sub>, TMS as internal standard)

| Compound <b>3</b>         | Pyridazine (s, 2H) | Double bonds (AB, 4H) <sup>a</sup> |      | Benzene rings         | Alkoxy groups                                |  |                           |  |
|---------------------------|--------------------|------------------------------------|------|-----------------------|--|--|---------------------------|--|
|                           |                    | α-CH                               | β-CH | $(AA'BB', ABC, A_2)$  | OCH <sub>3/2/1</sub>                         | CH <sub>2</sub> (m)                            | $CH_{3}(t)$               |  |
| a                         | 7.54               | 7.23                               | 7.56 | 6.92, 7.53 (8H)       | 3.84 (s, 6H)                                 |  |                           |  |
| b                         | 7.54               | 7.21                               | 7.58 | 6.91, 7.52 (8H)       | 4.06 (q, 4H)                                 |  | 1.42 (6H)                 |  |
| с                         | 7.53               | 7.22                               | 7.56 | 6.90, 7.52 (8H)       | 3.99 (t, 4H)                                 | 1.78 (4H), 1.49 (4H)                           | 0.98 (6H)                 |  |
| d                         | 7.54               | 7.22                               | 7.53 | 6.91, 7.56 (8H)       | 3.98 (t, 4H)                                 | 1.79 (4H), 1.45 (4H), 1.36 (8H)                | 0.90 (6H)                 |  |
| e                         | 7.53               | 7.22                               | 7.56 | 6.90, 7.52 (8H)       | 3.98 (t, 4H)                                 | 1.78 (4H), 1.45 (4H), 1.27 (16H)               | 0.89 (6H)                 |  |
| f                         | 7.54               | 7.23                               | 7.56 | 6.90, 7.52 (8H)       | 3.78 (t, 4H)                                 | 1.78 (4H), 1.45 (4H), 1.22 (24H)               | 0.89 (6H)                 |  |
| $\mathbf{g}^{\mathrm{b}}$ | 7.50               | 7.21                               | 7.53 | 6.88, 7.48 (8H)       | 3.95 (t, 4H)                                 | 1.75 (4H), 1.40 (4H), 1.22 (32H)               | 0.83 (6H)                 |  |
| ĥ                         | 7.51               | 7.21                               | 7.60 | 6.93, 7.53 (8H)       | 3.98 (t, 4H)                                 | 1.80 (4H), 1.45 (4H), 1.25 (56H)               | 0.89 (6H)                 |  |
| ij                        | 7.53               | 7.23                               | 7.57 | 6.88, 7.51 (8H)       | 4.39 (m, 2H)                                 | 1.75 (2H), 1.42 (4H), 1.31 (20H)<br>1.55 (2H)  | 0.87 (6H)<br>1.28 (d, 6H) |  |
| k                         | 7.56               | 7.23                               | 7.49 | 6.86, 7.08, 7.17 (6H) | 4.02 (t, 4H)<br>4.05 (t, 4H)                 | 1.85 (8H), 1.44 (8H), 1.27 (16H)               | 0.88 (12H)                |  |
| lp                        | 7.53               | 7.16                               | 7.46 | 6.81, 7.05, 7.10 (6H) | 3.93 (t, 4H)<br>3.97 (t, 4H)                 | 1.73 (8H), 1.39 (8H), 1.18 (64H)               | 0.80 (12H)                |  |
| m                         | 7.55               | 7.23                               | 7.53 | 6.88, 7.08, 7.11 (6H) | 4.02 (t, 4H)<br>4.05 (t, 4H)                 | 1.85 (8H), 1.49 (8H), 1.28 (96H)               | 0.88 (12H)                |  |
| n                         | 7.58               | 7.25                               | 7.51 | 6.87, 7.09, 7.16 (6H) | 3.92 (s, 6H)<br>4.05 (t, 4H)                 | 1.85 (4H), 1.45 (4H), 1.25 (32H)               | 0.89 (6H)                 |  |
| 0                         | 7.61               | 7.31                               | 7.52 | 6.83 (4H)             | 3.89 (s, 6H)<br>3.89 (s, 12H)                |  |                           |  |
| р                         | 7.59               | 7.27                               | 7.46 | 6.79 (4H)             | 3.97 (t, 4H)<br>4.01 (t, 8H)                 | 1.74 (4H), 1.45 (12H), 1.34 (24H)<br>1.81 (8H) | 0.88 (18H)                |  |
| q                         | 7.59               | 7.28                               | 7.46 | 6.80 (4H)             | 3.98 (t, 4H)<br>4.00 (t, 8H)                 | 1.75 (4H), 1.45 (12H), 1.28 (72H)<br>1.85 (8H) | 0.88 (18H)                |  |
| r                         | 7.59               | 7.28                               | 7.47 | 6.79 (4H)             | 3.97 (t, 4H)<br>4.01 (t, 8H)                 | 1.74 (4H), 1.48 (12H), 1.25 (96H)<br>1.82 (8H) | 0.87 (18H)                |  |
| s                         | 7.61               | 7.32                               | 7.54 | 6.84 (4H)             | 3.88 (s, 12H)<br>4.00 (t, 4H)                | 1.72 (4H), 1.45 (4H), 1.29 (32H)               | 0.88 (6H)                 |  |
| t                         | 7.60               | 7.29                               | 7.49 | 6.80, 6.81 (AB, 4H)   | 3.88 (s, 6H)<br>4.02 (t, 4H)<br>4.05 (t, 4H) | 1.85 (4H), 1.45 (8H), 1.24 (64H)<br>1.72 (4H)  | 0.88 (12H)                |  |

<sup>a</sup> <sup>3</sup>*J*=16.2±0.2 Hz.

<sup>b</sup> Measurement in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 50 °C.

as the first heating curves. The onset temperatures (Fig. 3) of the phase transitions can differ a little bit, because the peak shape of the second heating curve can be somewhat different from that of the first heating curve.

A butoxy chain is already sufficient for the self-organization in a smectic phase. The strongly fluctuating textures of the nematic systems are then transformed on cooling to textures in which 'Schlieren' regions can be seen as well as fan-shaped regions. Homeotropic and homogenous oriented domains cause this coexistence, which permits the assignment of the smectic phases as S<sub>c</sub>.<sup>25</sup> Further cooling leads for  $n \ge 6$  to another phase transition with a very small enthalpy  $\Delta H$  (Figs. 2 and 3). The spacial impression of the fan-shaped structures disappears, transverse fissures appear and a fine granulation becomes evident. The 'Schlieren' texture in the homeotropic regions becomes in wide areas mosaic-like. Such typical changes are based on the formation of hexagonal positions of the mesogens, which were before fairly mobile in the S<sub>C</sub> phase. The molecules can be tilted in the direction of a tip or a plane of the hexagon. Without further distinction between these tilted hexatic phases, we designate this phase as  $S_{F/I}$ .<sup>25</sup> Figure 4 illustrates as an example the phase behavior of 3g(n=12). The isotropic melt (I) is transformed at 259.4  $^{\circ}$ C (532.5 K) to the S<sub>C</sub> phase with an exothermic transition enthalpy  $\Delta H$  of  $-7 \text{ kJ mol}^{-1}$ . At 170.6 °C (443.7 K), another exothermic phase transition ( $\Delta H = -2 \text{ kJ mol}^{-1}$ ) occurs, which causes the above-mentioned and in Figure 4 visible texture changes for the process  $S_C \rightarrow S_{F/I}$ . Finally, the now more viscous phase crystallizes at 129.7 °C (402.8 K) with a strong exothermic transfer enthalpy  $\Delta H = -34$  kJ mol<sup>-1</sup>.

Interestingly **3h** (*n*=18) does not show the direct transition  $I \rightarrow S_C$ , which is observed for **3e-g** (Fig. 3). A drastically enhanced viscosity indicates at 216 °C that the isotropic appearance of the probe originates from a cubic mesophase, whose transfer to the

 $S_C$  phase at 201  $^\circ C$  (onset temperature) is characterized by the typical generation of rhombic domains (upper part of Fig. 5).^{26}

The S<sub>C</sub> phases of **3a–h**, which are stable in a wide temperature range, stimulated us to introduce a chirality center in the alkoxy chains and to study the possibility of ferro- or antiferroelectric phases. Therefore, we synthesized **3i** [racemate of (*R*,*R*) and (*S*,*S*) configurations and *meso* form (*R*,*S*)] and **3j**, the pure (*S*,*S*) isomer. The branching of the alkoxy chains led to a drastic decrease of the phase transition temperatures. The (*S*,*S*) isomer **3j** shows in the second DSC heating curve, the formation of a smectic phase at 112 °C ( $\Delta H$ =22 kJ mol<sup>-1</sup>). The cooling process I→S has an onset temperature of 138 °C ( $\Delta H$ =−2 kJ mol<sup>-1</sup>) and crystallization occurs at 89 °C ( $\Delta H$ =−21 kJ mol<sup>-1</sup>). Close to the crystallization/melting peak toward lower temperatures are transitions between different crystalline phases.

The racemate **3i** melts at 124 °C ( $\Delta H=25$  kJ mol<sup>-1</sup>) to the S<sub>B</sub> phase, which forms the isotropic phase at 144 °C ( $\Delta H=3$  kJ mol<sup>-1</sup>) and cooling leads then back at 130 °C ( $\Delta H=-2$  kJ) to the S<sub>B</sub> phase and at 106 °C ( $\Delta H=-23$  kJ mol<sup>-1</sup>) to the first crystalline phase. (The DSC processes were studied with rates of 10 and 3 K min<sup>-1</sup>.) The assignment of the smectic phase to the hexatic S<sub>B</sub> order is based on typical mosaic structures of the texture.<sup>27</sup>

The slight modification of the alkoxy chains by introduction of an  $\alpha$ -CH<sub>3</sub> group permits the molecules to adopt an arrangement parallel to the director of the smectic layer, so that S<sup>\*</sup><sub>C</sub>, S<sup>\*</sup><sub>CA</sub>, and S<sup>\*</sup><sub>F/I</sub> phases are not formed.

Increasing length of the alkoxy chains in **3a–h** provokes a decrease of the melting and clearing points, which is attended by a broadening of the mesophase range. Nevertheless, all phase transition temperatures of **3a–h** are above 130 °C, which is too high for any application. Therefore, we introduced further alkoxy groups in 3- and 5-position of the terminal benzene rings. Compound **3k** 

Table 2 <sup>13</sup>C NMR data of the pyridazines **3a–3g**, and **3i**,**j–3t** ( $\delta$  values in CDCl<sub>3</sub>, TMS as internal standard)

| Compound <b>3</b>         | Pyridazine |       | Double bonds |       | Benzene rings |       |       | Alkoxy groups        |   |              |
|---------------------------|------------|-------|--------------|-------|---------------|-------|-------|----------------------|---|--------------|
|                           | СН         | Cq    | α-CH         | β-CH  | СН            | Cq    | CqO   | OCH <sub>3/2/1</sub> | CH <sub>2</sub> <sup>a</sup>                | CH3          |
| a                         | 123.5      | 156.4 | 123.1        | 133.8 | 114.3, 128.7  | 129.0 | 160.3 | 55.4                 |   |              |
| b                         | 123.5      | 156.4 | 123.0        | 133.8 | 114.8, 128.7  | 128.8 | 159.7 | 63.6                 |   | 14.8         |
| с                         | 123.5      | 156.4 | 123.0        | 133.8 | 114.8, 128.7  | 128.8 | 159.9 | 67.8                 | 19.2, 31.1                                  | 13.8         |
| d                         | 123.5      | 156.4 | 123.0        | 133.8 | 114.8, 128.6  | 128.7 | 159.9 | 68.1                 | 22.6, 25.7, 29.2, 31.6                      | 14.0         |
| e                         | 123.5      | 156.5 | 123.1        | 133.9 | 114.9, 128.6  | 128.9 | 160.0 | 68.2                 | 22.6, 26.0, 29.2, 29.3, 29.4,<br>31.8       | 14.0         |
| f                         | 123.5      | 156.7 | 123.0        | 133.9 | 114.9, 128.6  | 128.7 | 159.9 | 68.1                 | 22.6, 26.0, 29.2, 29.3, 29.4,<br>29.6, 31.9 | 13.9         |
| $\mathbf{g}^{\mathrm{b}}$ | 124.6      | 156.6 | 122.9        | 134.6 | 115.4, 129.0  | 128.9 | 160.4 | 68.6                 | 22.9, 26.3, 29.5, 29.6, 29.8,<br>29.9, 32.2 | 14.4         |
| ij                        | 123.4      | 156.4 | 123.0        | 133.8 | 116.0, 128.7  | 128.6 | 159.0 | 74.0                 | 22.6, 25.5, 29.2, 31.8, 36.4                | 14.1<br>19.7 |
| k                         | 123.4      | 156.5 | 123.1        | 134.1 | 111.7, 121.4  | 129.2 | 153.3 | 69.2                 | 22.6, 25.6, 25.7, 29.2, 29.3,               | 14.1         |
|                           |            |       |              |       | 113.4         |       | 149.4 | 69.4                 | 31.6  |              |
| 1                         | 124.1      | 156.6 | 123.1        | 134.9 | 113.6, 121.9  | 129.6 | 150.0 | 69.9                 | 22.9, 26.3, 26.4, 29.7, 29.8,               | 14.4         |
|                           |            |       |              |       | 114.7         |       | 151.1 | 71.1                 | 29.9, 30.0, 31.1                            |              |
| m                         | 123.4      | 156.5 | 123.3        | 134.3 | 112.8, 121.4  | 129.7 | 149.8 | 69.6                 | 22.6, 26.0, 29.3, 29.4, 29.6,               | 14.0         |
|                           |            |       |              |       | 114.3         |       | 150.7 | 69.8                 | 31.9  |              |
| n                         | 123.4      | 156.5 | 121.4        | 134.2 | 109.8, 121.4  | 129.2 | 149.8 | 56.1                 | 22.7, 26.0, 29.2, 29.3, 29.4,               | 14.1         |
|                           |            |       |              |       | 112.9         |       | 149.9 | 69.2                 | 29.5, 29.6, 29.7, 32.0                      |              |
| 0                         | 123.5      | 156.4 | 124.7        | 134.4 | 104.6         | 131.7 | 139.4 | 56.2                 |   |              |
|                           |            |       |              |       |               |       | 153.6 | 61.0                 |   |              |
| р                         | 123.4      | 156.4 | 124.4        | 134.5 | 105.8         | 131.2 | 139.3 | 69.1                 | 22.6, 25.7, 29.3, 30.2, 31.5,               | 14.1         |
|                           |            |       |              |       |               |       | 153.2 | 73.5                 | 31.7  |              |
| q                         | 123.4      | 156.4 | 124.4        | 134.6 | 106.1         | 131.2 | 139.6 | 69.3                 | 22.6, 26.1, 29.3, 29.4, 29.6,               | 14.1         |
|                           |            |       |              |       |               |       | 153.4 | 73.6                 | 29.7, 30.9, 31.9                            |              |
| r                         | 123.4      | 156.5 | 124.4        | 134.6 | 106.1         | 131.3 | 139.6 | 69.3                 | 22.7, 26.1, 29.3, 29.4, 29.6,               | 14.1         |
|                           |            |       |              |       |               |       | 153.4 | 73.6                 | 29.7, 30.4, 31.9                            |              |
| s                         | 123.5      | 156.4 | 124.6        | 134.5 | 104.8         | 131.4 | 138.8 | 56.3                 | 22.7, 25.9, 29.4, 29.5, 29.7,               | 14.1         |
|                           |            |       |              |       |               |       | 153.8 | 73.7                 | 31.2  |              |
| t                         | 123.4      | 156.5 | 124.5        | 134.5 | 104.7         | 131.6 | 139.1 | 56.3                 | 22.7, 26.0, 26.1, 29.3, 29.4,               | 14.1         |
|                           |            |       |              |       | 106.1         |       | 153.3 | 69.3                 | 29.5, 29.6, 30.3, 31.9                      |              |
|                           |            |       |              |       |               |       | 153.9 | 73.7                 |   |              |

<sup>a</sup> The CH<sub>2</sub> signals of long alkoxy chains are often superimposed.

<sup>b</sup> Measurement in  $C_2D_2Cl_4$  at 50 °C.

surement in CDCl<sub>3</sub>, TMS as internal standard).

240 220 T / °C 200 180

160



Figure 1.  $^{1}$ H and  $^{13}$ C NMR data of the styrylpyridazine substructure of **3a–t**. (Mea-

with two hexyloxy groups on each benzene ring shows in the DSC at 128.0 °C (onset temperature) a relatively sharp melting point. The crystalline phase passes over into the isotropic melt ( $\Delta H$ = 52 kJ mol<sup>-1</sup>). Compounds **31** (p-OC<sub>12</sub>H<sub>25</sub> and m-OC<sub>12</sub>H<sub>25</sub>) and **3m**  $(p-OC_{16}H_{33} \text{ and } m-OC_{16}H_{33})$  behave in the first and second heating

3g 3h 3a 3d 320 300 280 260 K SFA 140 120 7 8 9 18 2 3 4 5 6 10 11 12 1 n

Figure 2. Phases of (*E,E*)-3,6-bis[2-(4-alkoxyphenyl)vinyl]pyridazines 3a-3h (OC<sub>n</sub>H<sub>2n+1</sub>, n=1, 2, 4, 6, 8, 10, 12, 18). K: crystalline, N: nematic, S<sub>C</sub>, S<sub>F/I</sub>: smectic, Cub: cubic, and I: isotropic phase. (The transition temperatures refer to the heating curve in the DSC).

| 3a | K $\frac{272 (38)}{250 (-29)}$ N $\xrightarrow{\sim 310}$ I (decomp.)  |
|----|--|
| 3b | $K \xrightarrow{230 (18)}{220 (-15)} N \xrightarrow{-310} I (decomp.)$   |
| 3c | $K \; \frac{224\; (20)}{209\; (-19)} \; S_{C} \; \; \frac{258\; (3)}{256\; (-3)} \; N \; \stackrel{\sim 310}{\longrightarrow} \; I \; (decomp.)$                               |
| 3d | $K \xrightarrow{161 (19)}{149 (-19)} S_{F/I} \xrightarrow{170 (2)}{168 (2)} S_C \xrightarrow{283 (3)}{282 (-3)} N \xrightarrow{\sim 305} I (decomp.)$                          |
| 3e | $K = \frac{158 (19)}{150 (-21)} S_{F/I} = \frac{170 (1)}{163 (-1)} S_C = \frac{285 (a)}{280 (a)} I$  |
| 3f | $\label{eq:K} K \; \frac{151\;(27)}{145\;(-26)} \;\; S_{F/I} \;\; \frac{183\;(2)}{182\;(-1)} \;\; S_{C} \;\; \frac{293\;(a)}{292\;(a)} \;\; I$                                 |
| 3g | $K \; \frac{139\; (36)}{130\; (-34)} \;\; S_{F/I} \;\; \frac{168\; (2)}{171\; (-2)} \;\; S_{C} \;\; \frac{266\; (10)}{259\; (-7)} \;\; I$                                      |
| 3h | $K \; \frac{136\; (44)}{130\; (-46)} \;\; S_{F/I} \;\; \frac{152\; (3)}{156\; (-2)} \;\; S_{C} \;\; \frac{211\; (2)}{201\; (-2)} \;\; Cub \frac{223\; (2)}{216\; (-2)} \;\; I$ |

Figure 3. Transitions of 3a-3h between crystalline (K), smetic (S<sub>F/I</sub>, S<sub>C</sub>), nematic (N), and isotropic (I) phases. Upper transition: onset temperature of second heating curve, °C, ( $\Delta H$  in kJ mol<sup>-1</sup>); lower transition: onset temperature of second cooling curve, °C,  $(\Delta H \text{ in kJ mol}^{-1})$ ; (a)  $\Delta H$  not determined.



**Figure 4.** Characterization of the mesophases of 3,6-bis[2-(4-dodecyloxyphenyl)-vinyl]pyridazine (**3g**): (a) DSC diagram (second heating curve, 10 K min<sup>-1</sup>), (b) cooling curve, 10 K min<sup>-1</sup>, and (c) textures obtained in the polarization microscope at 417 and 473 K, respectively. (Scale 1:115).

curves similarly. They show at 122.2 °C ( $\Delta H=92 \text{ kJ} \text{ mol}^{-1}$ ) and 122.6 °C ( $\Delta H=117.5 \text{ kJ} \text{ mol}^{-1}$ ), respectively, such K  $\rightarrow$  I transitions, but in their cooling curves, smectic phases can be observed in relatively narrow temperature ranges (**3I**: *T* [°C] 123.7–106.4,  $\Delta H$  [kJ mol<sup>-1</sup>] 4 and 96; **3m**: *T* [°C] 122.7–108.9,  $\Delta H$  [kJ mol<sup>-1</sup>] 4 and 124). The textures, obtained for these smectic phases, point to an S<sub>A</sub> character.<sup>28</sup> The models in Figure 6 illustrate the influence, which the additional, long alkoxy chains in *m*-position can have on the orientation of the molecules in the smectic phases. Whereas the *transoid* arrangement of the two olefinic double bonds is favorable for the S<sub>C</sub> phase, the *cisoid* arrangement seems to be more

![](_page_4_Picture_4.jpeg)

**Figure 5.** Upper part: formation of the texture of the S<sub>C</sub> phase from the cubic phase of **3h** at 213 °C, scale 1:90. Lower part: texture of the S<sub>E</sub> phase of **3n**, measured at 141 °C close to the clearing point, scale 1:90.

appropriate for the  $S_A$  phase. The increased cylinder volume, caused by the additional alkoxy chains, enhances the chances of the *cisoid* conformation.

In contrast to the monotropic mesophase formation of **31** and **3m**, **3n**  $(p-OC_{12}H_{25}$  and  $m-OCH_3)$  exhibits enantiotropic phase transitions. The crystalline state is transformed in the second heating curve at 61 °C ( $\Delta H$ =33 kJ mol<sup>-1</sup>) to the smectic phase and at 145 °C  $(\Delta H=50 \text{ kJ mol}^{-1})$  the isotropic melt is generated. The cooling process (measured with the same rate of 10 K min<sup>-1</sup>) exhibits the  $I \rightarrow S$ transition at 135 °C ( $\Delta H$ =-46 kJ mol<sup>-1</sup>) and the formation of the crystalline state (S  $\rightarrow$  K) at 56 °C ( $\Delta H$ =-33 kJ mol<sup>-1</sup>). It is remarkable that the smectic mesophase of **3n** exists in a much broader temperature range than the mesophases of **31** and **3m**. Moreover, the transition enthalpy  $\Delta H$  of **3n** is higher for the clearing process  $S \rightarrow I$ than for the melting process. These results demonstrate, that the smectic phase of **3n** is highly ordered. The texture of **3n** contains a bulky mosaic structure, which points to an S<sub>E</sub> phase.<sup>29</sup> Figure 5 (lower part) shows that this texture is preserved till the clearing process starts. Compounds **30–3t** have alkoxy groups in *p*- and both *m*-positions of the terminal benzene rings. The hexamethoxy system 30 is a yellow solid, which decomposes above 170 °C. Compounds **3p** and **3q** exist at room temperature in highly viscous smectic phases with clearing points at 77 and 96 °C, respectively. Crystallization cannot be observed in DSC down to -70 °C. Figure 7 summarizes the phase transitions of **3r-t**. Whereas the transition

![](_page_5_Figure_2.jpeg)

**Figure 6.** Model for the arrangement of dialkoxy-substituted bis(styryl)pyridazines **3c-h** in smectic S<sub>C</sub> phases (*transoid* double bonds in narrow cylindric volumina) and tetralkoxy-substituted bis(styryl)pyridazines (**3l-n**) in smectic S<sub>A</sub> phases (*cisoid* double bonds in wider cylindric volumina).

![](_page_5_Figure_4.jpeg)

**Figure 7.** Transitions of **3r**, **3s**, and **3t** between crystalline (K), smectic (S), and isotropic (I) phases. Upper transition: second heating curve in the DSC, onset temperature in °C (endothermic  $\Delta H$  in kJ mol<sup>-1</sup>); lower transition: cooling curve in the DSC, onset temperature in °C (exothermic  $\Delta H$  in kJ mol<sup>-1</sup>). The rate of all measurements was 10 K min<sup>-1</sup>.

enthalpies  $\Delta H$  of 2,6-bis[2-(3,4,5-tridodecyloxyphenyl)vinyl]pyridazine (**3r**) resemble the 'normal' behavior of compounds **3a–h** with a high  $\Delta H$  for K  $\rightarrow$  S and a much lower  $\Delta H$  for S  $\rightarrow$  I, but **3s** shows like **3n** the opposite behavior, a much larger  $\Delta H$  for S  $\rightarrow$  I than for K  $\rightarrow$  S, which is again a strong indication for a highly ordered smectic phase. The DSC measurements of **3t** were much more complicated, because the second heating and cooling curves exhibit several closely lying smectic phases. The endothermic behavior of the heating curve between 30 and 54 °C is interrupted by an exothermic part (reentrant phase).

According to the temperature range of the LC phases, compounds **3p**–**3s** are certainly the most suitable for applications, since they exist at room temperature in smectic phases. In principle such phasmidic systems could exist also in a columnar arrangement. In order to exclude this possibility, we made for **3r** an X-ray scattering measurement, which is shown in Figure 8. The highest peak corresponds to a distance of 29.2 Å, which represents the thickness of a smectic layer S<sub>A</sub> with highly flexible chains and relatively low order. (Molecular models reveal that **3r** would have a length of about 45 Å, in the maximum stretched form.) Reflections for columnar or higher ordered smectic phases could not be found. The halo at  $2\theta$ =20° corresponds to 4.5 Å and represents the average intermolecular distance. The texture of **3r** is in accordance with an S<sub>A</sub> phase.<sup>24b,28</sup>

![](_page_5_Figure_8.jpeg)

Figure 8. X-ray scattering of compound 3r in the S<sub>A</sub> phase at room temperature.

#### 2.3. Light-sensitivity of the (E,E)-3,6-bis(styryl)pyridazines 3

Compounds **3a-t** exhibit strong long-wavelength absorption bands with maxima between 360 and 380 nm. (E,E)-3,6-Bis[2-(4hexyloxyphenyl)vinyl]pyridazine (**3d**), for example, has a  $\lambda_{max}$ value of 372 nm ( $\varepsilon_{max}$ =52,000 L mol<sup>-1</sup> cm<sup>-1</sup>) in benzene. The absorption of light of the visible and near UV region renders these compounds light-sensitivity. Figure 8 shows UV/vis spectra of the irradiation of **3d** in a  $1.96 \times 10^{-4}$  M solution in oxygen-free benzene with a Hanovia medium pressure lamp equipped with a Pyrex filter  $(\lambda > 290 \text{ nm})$ . Isosbestic points as well as the <sup>1</sup>H NMR reaction spectra reveal a clean process (E,E)-**3d**  $\rightleftharpoons$  (E,Z)-**3d**. The principally possible further isomer (Z,Z)-3d can be excluded. According to the <sup>1</sup>H NMR spectroscopy, the photostationary state has—under the above-mentioned reaction conditions—the composition (E,E)-3d/ (*E*,*Z*-**3d**)=54:46. This ratio was used to calculate the absorption spectrum of the pure (E,Z) configuration of **3d**, which is shown in Figure 9.

The <sup>1</sup>H NMR spectrum of (*E*,*Z*)-**3d** corresponds to the reduced symmetry. Table 3 shows the comparison of the data of (*E*,*E*)-**3d** and (*E*,*Z*)-**3d**.<sup>30</sup>

Now the crucial question is, how can these isomerization processes be used in materials science? (E,Z) Configured 3,6-bis(styryl)-pyridazines **3** are certainly not suitable for LC phases. Even small

![](_page_5_Figure_14.jpeg)

**Figure 9.** UV/vis absorbance *A* of a  $1.96 \times 10^{-4}$  M solution of **3d** in benzene: (*E*,*E*)- and (*E*,*Z*)-**3d**, Ph.St.: photostationary state (*E*,*E*)/(*E*,*Z*)=54:46.

| Table 3   |       |
|---|-------|
| <sup>1</sup> H NMR data of ( <i>E</i> . <i>E</i> )- <b>3d</b> and ( <i>E</i> . <i>Z</i> )- <b>3d</b> ( $\delta$ values in C <sub>6</sub> D <sub>6</sub> . TMS as internal stand | lard) |

| Compound                           |   | Pyridazine ring         | (E)-Styryl group         |                      | (Z)-Styryl group         |                      | OCH <sub>2</sub> |
|------------------------------------|---|-------------------------|--------------------------|----------------------|--------------------------|----------------------|------------------|
|                                    |   |                         | Double bond              | Benzene ring         | Double bond              | Benzene ring         |                  |
| (E,E)- <b>3d</b>                   | δ<br>Spin system<br><sup>3</sup> J [Hz] | 6.81<br>A <sub>2</sub>  | 7.36, 7.69<br>AB<br>16.1 | 6.83, 7.37<br>AA'BB' |                          |                      | 3.61             |
| ( <i>E</i> , <i>Z</i> )- <b>3d</b> | δ<br>Spin system<br><sup>3</sup> J [Hz] | 6.53, 6.99<br>AB<br>8.2 | 7.29, 7.53<br>AB<br>16.1 | 6.80, 7.30<br>AA'BB' | 6.72, 7.03<br>AB<br>12.4 | 6.73, 7.18<br>AA'BB' | 3.59, 3.61       |

portions of 'wrong' configuration can disturb the self-organization of mesogens. Processes  $I \rightarrow LC$ , in which an isotropic phase is transformed to an LC phase by the photoisomerization (*E*,*Z*)-**3**  $\rightarrow$  (*E*,*E*)-**3** of a certain content of 'wrong' configuration, seem to be easily feasible. However, the opposite process (*E*,*E*)-**3**  $\rightarrow$  (*E*,*Z*)-**3** may cause difficulties in self-organized, constrained phases. The higher the order of such LC phases is, the less likely are such photoisomerizations. The great manifold of smectic phases of (*E*,*E*)-**3** provides in this context a very interesting research area.<sup>31</sup>

#### 3. Conclusion

A large variety of 3,6-bis(styryl)pyridazines **3a-t** with 2, 4 or 6 alkoxy groups on the terminal benzene rings were prepared as pure (E,E)-isomers by using kinetically controlled Siegrist reactions. Even short alkoxy chains (OCH<sub>3</sub> or OC<sub>2</sub>H<sub>5</sub>) are sufficient to induce selforganization in LC phases. Depending on the number and length of the  $OC_nH_{2n+1}$  chains, nematic (N), smectic (S<sub>A</sub>, S<sub>B</sub>, S<sub>C</sub>, S<sub>E</sub>, and S<sub>I/F</sub>), and cubic (Cub) orders were assigned to the thermotropic liquid crystals. The characterization of the mesophases is predominantly based on DSC measurements and observations of typical textures in the polarization microscope. The conjugated structure with a central pyridazine ring renders compounds (*E*,*E*)-**3** not only the character of a rigid mesogen with a high aggregation tendency, it represents also a chromophore (absorption at the UV/vis border), which conveys compounds **3** a highly photosensitive character for  $(E,E) \rightleftharpoons (E,Z)$ isomerization reactions. The application of such processes in materials science will be reported in a forthcoming publication.

#### 4. Experimental

#### 4.1. General

Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. The DSC measurements were performed on a Perkin–Elmer DSC 7. The IR reaction control was made in neat phase with a Beckman Acculab spectrometer. A Zeiss MCS 224/234 diode array spectrometer was used for the UV/vis spectroscopy. The Bruker spectrometers AC 200, AC 300, and AM 400 served for the obtention of the <sup>1</sup>H and <sup>13</sup>C NMR spectra. CDCl<sub>3</sub> was used as solvent and TMS as internal standard—if not otherwise stated. The mass spectra (EI and FD) were obtained on a Finnigan MAT 95. Polarization microscopy was performed with a Leitz Ortholux II microscope/Mettler FP-52 heating system. Small and wide-angle X-ray scattering was measured with a Siemens D-500 diffractometer (DACO-MP computer interface, Cu K $\alpha$ ). The elemental analyses were made in the Microanalytical Laboratory of the Institute of Organic Chemistry, University of Mainz.

### **4.2.** General procedure for the preparation of the Schiff bases (*N*-benzylideneanilines) 10a–t

The condensation reaction of the substituted benzaldehydes 8a-t (25 mmol) and aniline (9) (3.26 g, 35 mmol) was performed at

80 °C in the absence of a solvent. The vacuum of 2.0–2.1 kPa served for the removal of the generated water. IR or TLC control indicated the end of the quantitative reaction. The excess aniline was then removed at a reduced pressure of 0.1 kPa. The light yellow residue could directly be used for the subsequent reaction step.

The majority of the Schiff bases **10a**–**t** was identified by comparison with authentic samples: **10a**, <sup>32</sup> **10b**, <sup>33</sup> **10c**, <sup>34</sup> **10d**, <sup>35</sup> **10e**, <sup>36</sup> **10f**, <sup>37</sup> **10g**, <sup>3</sup> **10h**, <sup>38</sup> **10k**, <sup>39</sup> **10l**, <sup>40</sup> **10m**, <sup>40</sup> **10o**, <sup>20</sup> **10p**, <sup>41</sup> and **10r**. <sup>40</sup>

#### 4.2.1. N-[4-(1-Methylheptyloxy)benzylidene]aniline (10i)

Yellowish oil, yield: 7.73 g (quantitative) obtained from aldehyde **8i**.<sup>42 1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, 3H, CH<sub>3</sub>), 1.30 (d, 3H, CH<sub>3</sub>), 1.32 (m, 6H, CH<sub>2</sub>), 1.38 (m, 2H, CH<sub>2</sub>), 1.59 (m, 1H, CH<sub>2</sub>), 1.73 (m, 1H, CH<sub>2</sub>), 4.45 (m, 1H, CH), 6.95/7.82 (AA'BB', 4H, *p*-phenylene), 7.18 (m, 3H, phenyl), 7.38 (m, 2H, phenyl), 8.37 (s, 1H, CHN); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.0, 19.6 (CH<sub>3</sub>), 22.5, 25.3, 29.1, 31.7, 36.3 (CH<sub>2</sub>), 74.0 (CH), 115.7, 120.8, 125.4, 129.0, 130.5 (aromat. CH), 128.8, 152.2, 162.0 (aromat. C<sub>q</sub>), 159.6 (CHN); EIMS: *m/z* (%) 309 (16) [M<sup>++</sup>], 197 (100), 110 (67), 93 (77), 66 (29), 43 (28). Anal. Calcd for C<sub>21</sub>H<sub>27</sub>NO (309.5): C 81.51, H 8.79, N 4.53; found: C 81.27, H 8.68, N 4.41. The chiral compound (*S*)-**10** was obtained in the same way from the corresponding aldehyde (*S*)-**8**<sup>42</sup>

#### 4.2.2. N-(4-Dodecyloxy-3-methoxybenzylidene)aniline (10n)

The preparation of **10n** was started with the alkylation of 4-hydroxy-3-methoxybenzaldehyde (vanillin) with 1-bromododecane to afford 4-dodecyloxy-3-methoxybenzaldehyde (8n),<sup>43</sup> which melted at 60 °C (lit.<sup>41</sup> 57 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.82 (t, 3H, CH<sub>3</sub>), 1.23 (m, 16H, CH<sub>2</sub>), 1.45 (m, 2H, CH<sub>2</sub>), 1.85 (m, 2H, CH<sub>2</sub>), 3.88 (s, 3H, OCH<sub>3</sub>), 4.05 (t, 2H, OCH<sub>2</sub>), 6.92/7.39/7.42 (ABC, 3H, aromat. H), 9.81 (s, 1H, CHO); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.6, 25.8, 28.9, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9 (CH<sub>2</sub>), 56.0 (OCH<sub>3</sub>), 69.2 (OCH<sub>2</sub>), 110.4, 111.5, 126.6 (aromat. CH), 129.9, 149.9, 154.2 (aromat. C<sub>a</sub>), 190.7 (CHO). The general procedure, described before, afforded then a quantitative yield of 10n (9.88 g from 8.0 g aldehyde 8n), which is a yellow solid and melted at 40 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.82 (t, 3H, CH<sub>3</sub>), 1.23 (m, 16H, CH<sub>2</sub>), 1.45 (m, 2H, CH<sub>2</sub>), 1.85 (m, 2H, CH<sub>2</sub>), 3.98 (s, 3H, OCH<sub>3</sub>), 4.08 (t, 2H, OCH<sub>2</sub>), 6.92 (m, 1H), 7.20 (m, 3H), 7.29 (m, 1H), 7.49 (m, 2H), 7.53 (s, 1H) [aromat. H], 8.44 (s, 1H, CHN); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.6, 25.8, 28.9, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9 (CH<sub>2</sub>, partly superimposed), 56.0 (OCH<sub>3</sub>), 69.2 (OCH<sub>2</sub>), 109.5, 111.6, 120.8, 124.2, 126.5, 129.0 (aromat. CH), 129.3, 149.8, 151.7, 152.3 (aromat. C<sub>a</sub>), 159.8 (CHN); EIMS: *m*/*z* (%) 395 (21) [M<sup>+•</sup>], 65 (27), 54 (69), 43 (100). Anal. Calcd for C<sub>26</sub>H<sub>37</sub>NO<sub>2</sub> (395.6): C 78.94, H 9.43, N 3.54; found: C 78.85, H 9.54, N 3.73.

#### 4.2.3. N-(3,4,5-Tridecyloxybenzylidene)aniline (10q)

Aldehyde **8q**<sup>44</sup> gave a quantitative yield (16.2 g) of **10q**, a yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.89 (t, 9H, CH<sub>3</sub>), 1.28 (m, 36H, CH<sub>2</sub>), 1.49 (m, 6H, CH<sub>2</sub>), 1.78 (m, 2H, CH<sub>2</sub>), 1.83 (m, 4H, CH<sub>2</sub>), 4.03 (t, 2H, OCH<sub>2</sub>), 4.05 (m, 4H, OCH<sub>2</sub>), 7.12 (s, 2H), 7.18 (m, 2H), 7.21 (m, 1H), 7.37 (m, 2H) [aromat. H], 8.31 (s, 1H, CHN); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>3</sub>), 22.6, 26.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 30.3, 31.9 (CH<sub>2</sub>, partly superimposed), 69.2, 73.5 (OCH<sub>2</sub>), 107.3, 120.8, 125.6, 129.0

(aromat. CH), 131.3, 141.4, 152.2, 153.4 (aromat. C<sub>q</sub>), 160.1 (CHN); FD MS: m/z (%) 650 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>43</sub>H<sub>71</sub>NO<sub>3</sub> (650.0): C 79.45, H 11.01, N 2.15; found: C 79.11, H 10.92, N 2.19.

#### 4.2.4. N-(4-Dodecyloxy-3,5-dimethoxybenzylidene)aniline (10s)

Aldehyde **8s**<sup>45</sup> afforded a quantitative yield (10.60 g) of **10s**, a viscous yellow oil, which solidifies at 5 °C to a wax. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, 3H, CH<sub>3</sub>), 1.25 (m, 16H, CH<sub>2</sub>), 1.44 (m, 2H, CH<sub>2</sub>), 1.76 (m, 2H, CH<sub>2</sub>), 3.90 (s, 6H, OCH<sub>3</sub>), 4.02 (t, 2H, OCH<sub>2</sub>), 7.13 (s, 2H), 7.19 (m, 2H), 7.23 (m, 1H), 7.37 (m, 2H) [aromat. H], 8.32 (s, 1H, CHN); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>3</sub>), 22.6, 25.8, 29.3, 29.4, 29.6, 30.0, 31.8 (CH<sub>2</sub>, partly superimposed), 56.1 (OCH<sub>3</sub>), 73.5 (OCH<sub>2</sub>), 105.8, 120.8, 125.7, 129.0 (aromat. CH), 131.4, 140.3, 152.0, 153.7 (aromat. C<sub>q</sub>), 159.9 (CHN); EIMS: *m/z* (%) 425 (20) [M<sup>++</sup>], 257 (93), 182 (100), 57 (41), 43 (60). Anal. Calcd for C<sub>27</sub>H<sub>39</sub>NO<sub>3</sub> (425.3): C 76.20, H 9.24, N 3.29; found: C 76.03, H 9.35, N 3.50.

#### 4.2.5. N-(3,4-Didodecyloxy-5-methoxybenzylidene)-aniline (10t)

The aldehyde 8t was prepared from ethyl 3,4,5-trihydroxybenzoate, which was first twofold alkylated with 1-bromododecane to ethyl 3,4-didodecyloxy-5-hydroxybenzoate.<sup>40,46</sup> Iodomethane (1.56 g, 11.0 mmol) and the latter ester (4.97 g, 9.3 mmol) were refluxed together with K<sub>2</sub>CO<sub>3</sub> (4.1 g, 30.0 mmol) in 150 mL dry acetone for 2 days. The filtered solution was evaporated and the residue filtered over basic Al<sub>2</sub>O<sub>3</sub> (7×6 cm) with CH<sub>2</sub>Cl<sub>2</sub>. Ethyl 3,4didodecyloxy-5-methoxybenzoate (4.20 g, 82%) was obtained as colorless solid, which melted at 59 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, 6H, CH<sub>3</sub>), 1.25 (m, 32H, CH<sub>2</sub>), 1.34 (t, 3H, CH<sub>3</sub>), 1.43 (m, 4H, CH<sub>2</sub>), 1.72 (m, 2H, CH<sub>2</sub>), 1.79 (m, 2H, CH<sub>2</sub>), 3.85 (s, 3H, OCH<sub>3</sub>), 4.03 (t, 4H, OCH<sub>2</sub>), 4.35 (q, 2H, COOCH<sub>2</sub>), 7.24 (m, 2H, aromat. H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>, ester group), 22.7, 25.9, 26.1, 29.3, 29.4, 29.5, 29.7, 30.2, 31.9 (CH<sub>2</sub>, partly superimposed), 56.3 (OCH<sub>3</sub>), 60.9 (OCH<sub>2</sub>, ester group), 69.3, 73.5 (OCH<sub>2</sub>), 106.9, 108.3 (aromat. CH), 125.2, 142.1, 152.8, 153.3 (aromat. C<sub>q</sub>), 166.4 (CO). EIMS: *m*/*z* (%) 548 (52) [M<sup>+</sup>], 380 (32), 212 (100), 57 (45), 43 (64). Anal. Calcd for C<sub>34</sub>H<sub>60</sub>O<sub>5</sub> (548.8): C 74.41, H 11.02; found: C 74.54, H 11.08. The ester (4.0 g, 7.29 mmol), dissolved in 100 mL dry diethyl ether, was dropwise added at 5 °C to a suspension of LiAlH<sub>4</sub> (0.276 g, 7.29 mmol, twofold excess) in 50 mL dry diethyl ether. After refluxing for 3 h, 50 mL H<sub>2</sub>O was added and the mixture was neutralized with 2 M H<sub>2</sub>SO<sub>4</sub>. Extraction with diethyl ether and evaporation yielded the corresponding alcohol, 3,4-didodecyloxy-5-methoxybenzyl alcohol, which after recrystallization from toluene melted at 55 °C. Yield: 3.42 g (93%) colorless solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.88 (t, 6H, CH<sub>3</sub>), 1.25 (m, 32H, CH<sub>2</sub>), 1.42 (m, 4H, CH<sub>2</sub>), 1.71 (m, 2H, CH<sub>2</sub>), 1.78 (m, 2H, CH<sub>2</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 3.92 (t, 2H, OCH<sub>2</sub>), 3.95 (t, 2H, OCH<sub>2</sub>), 4.58 (s, 2H, CH<sub>2</sub>OH), 6.54 (s, 2H, aromat. H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.7, 26.0, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.2, 31.9 (CH<sub>2</sub>, partly superimposed), 56.2 (OCH<sub>3</sub>), 65.6 (CH<sub>2</sub>OH), 69.1, 73.5 (OCH<sub>2</sub>), 104.1, 105.5 (aromat. CH), 136.2, 137.3, 153.2, 153.8 (aromat. C<sub>0</sub>); EIMS: *m*/*z* (%) 506 (77) [M<sup>+•</sup>], 338 (40), 170 (100), 69 (21), 57 (47), 43 (73). Anal. Calcd for C32H58O4 (506.8): C 75.84, H 11.54; found: C 75.87, H 11.68. The substituted benzyl alcohol (3.20 g, 6.3 mmol) was then treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.58 g, 7.0 mmol) in 50 mL dry 1,4-dioxane. After 24 h stirring at ambient temperature, the mixture was filtered, evaporated, and purified by column filtration ( $7 \times 6$  cm SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>). Aldehyde **8t** was obtained as a colorless solid (3.0 g, 94%), which melted at 61  $^\circ\text{C}.$  <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, 6H, CH<sub>3</sub>), 1.24 (m, 32H, CH<sub>2</sub>), 1.42 (m, 4H, CH<sub>2</sub>), 1.73 (m, 2H, CH<sub>2</sub>), 1.81 (m, 2H, CH<sub>2</sub>), 3.88 (s, 3H, OCH<sub>3</sub>), 4.00 (t, 2H, OCH<sub>2</sub>), 4.03 (t, 2H, OCH<sub>2</sub>), 7.08 (s, 2H, aromat. H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.0 (CH<sub>3</sub>), 22.6, 25.9, 26.0, 29.2, 29.3, 29.4, 29.6, 30.2, 31.9 (CH<sub>2</sub>, partly superimposed), 56.2 (OCH<sub>3</sub>), 69.2, 73.6 (OCH<sub>2</sub>), 106.8, 108.1 (aromat. CH), 131.5, 143.5, 153.4, 154.0 (aromat. C<sub>a</sub>), 191.0 (CHO). EIMS: *m*/*z* (%) 504 (26) [M<sup>+•</sup>], 336 (28), 168 (100), 57 (42), 43 (57). Anal. Calcd for C<sub>32</sub>H<sub>56</sub>O<sub>4</sub> (504.8): C 76.14, H 11.18; found: C 76.08, H 11.17. Application of the above described general procedure furnishes then the aldimine **10t** in quantitative yield (3.0 g **10t** from 2.62 g **8t**). The yellow solid **10t** melts at 67 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, 6H, CH<sub>3</sub>), 1.25 (m, 32H, CH<sub>2</sub>), 1.45 (m, 4H, CH<sub>2</sub>), 1.75 (m, 2H, CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 3.91 (s, 3H, OCH<sub>3</sub>), 4.03 (t, 2H, OCH<sub>2</sub>), 4.06 (t, 2H, OCH<sub>2</sub>), 7.04 (m, 2H), 7.23 (m, 3H), 7.49 (m, 2H) [aromat. H], 8.32 (s, 1H, CHN); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>3</sub>), 22.6, 25.9, 26.0, 29.2, 29.3, 29.4, 29.6, 30.2, 31.6 (CH<sub>2</sub>, partly superimposed), 56.2 (OCH<sub>3</sub>), 69.6, 74.1 (OCH<sub>2</sub>), 106.8, 107.9, 121.1, 126.1, 129.2 (aromat. CH), 131.8, 141.4, 153.4, 154.1 (aromat. C<sub>q</sub>), 160.2 (CHN). EIMS: *m/z* (%) 579 (32) [M<sup>++</sup>], 71 (27), 57 (69), 43 (100). Anal. Calcd for C<sub>38</sub>H<sub>61</sub>NO<sub>3</sub> (579.9): C 78.71, H 10.60, N 2.42; found: C 78.48, H 10.71, N 2.21.

### **4.3.** General procedure for the preparation of the (*E*,*E*)-3,6-bis(styryl)pyridazines 3a–t

A slow stream of dry, oxygen-free N<sub>2</sub> was purged through a solution of 3,6-dimethylpyridazine **13**<sup>17,18</sup> (542 mg, 5.0 mmol) and aldimine **10a**–**t** (10.0 mmol) in 150 mL dry DMF. After about 30 min, KOH (3.3 g, 60 mmol) was added under vigorous stirring and the mixture was heated to 60 °C. After 1 h, 150 mL CH<sub>3</sub>OH was added at 0–5 °C. The precipitated product was washed with H<sub>2</sub>O and CH<sub>3</sub>OH and recrystallized. As indicated below, a column chromatography proved to be useful in some cases. (The normally low yields can be enhanced by an excess of **10a**–**t** and higher reaction temperatures, but the purification is then more difficult. In particular the (*E*,*Z*)-isomers are then enriched to an appreciable amount.)

#### 4.3.1. (E,E)-3,6-Bis[2-(4-methoxyphenyl)vinyl]pyridazine (3a)

Yield after recrystallization from toluene: 517 mg (30%) pale yellow needles, which melt to the nematic phase at 270 °C. EIMS: m/z (%) 344 (100) [M<sup>++</sup>], 115 (23). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (344.4): C 76.72, H 5.82, N 8.13; found: C 76.52, H 5.46, N 7.93.

#### 4.3.2. (E,E)-3,6-Bis[2-(4-ethoxyphenyl)vinyl]pyridazine (3b)

Yield after recrystallization from toluene: 150 mg (8%) pale yellow needles, which melt to the nematic phase at 230 °C. FD MS: m/z (%) 372 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> (372.4): C 77.39, H 6.49, N 7.52; found: C 77.31, H 6.47, N 7.61.

#### 4.3.3. (E,E)-3,6-Bis[2-(4-butoxyphenyl)vinyl]pyridazine (3c)

Yield after recrystallization from toluene: 170 mg (8%) pale yellow crystals, which melt to the nematic phase at 220 °C. EIMS: m/z (%) 428 (100) [M<sup>++</sup>], 372 (10), 57 (3). Anal. Calcd for C<sub>28</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub> (428.6): C 78.47, H 7.53, N 6.54; found: C 78.07, H 7.32, N 6.23.

#### 4.3.4. (E,E)-3,6-Bis[2-(4-hexyloxyphenyl)vinyl]pyridazine (3d)

Yield after recrystallization from toluene: 1.65 g (68%) pale yellow crystals, which melt at 160 °C to the smectic phase. EIMS: m/z (%) 484 (100) [M<sup>++</sup>], 400 (11), 316 (5). Anal. Calcd for C<sub>32</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub> (484.7): C 79.30, H 8.32, N 5.78; found: C 79.24, H 8.29, N 5.90.

#### 4.3.5. (E,E)-3,6-Bis[2-(4-octyloxyphenyl)vinyl]pyridazine (3e)

Yield after recrystallization from isopropanol: 136 mg (5%) pale yellow crystals, which melt at 155 °C to the smectic phase. EIMS: m/z (%) 540 (100) [M<sup>++</sup>], 428 (12), 57 (12). Anal. Calcd for C<sub>36</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub> (540.8): C 79.96, H 8.95, N 5.92; found: C 79.85, H 8.95, N 5.66.

#### 4.3.6. (E,E)-3,6-Bis[2-(4-decyloxyphenyl)vinyl]pyridazine (3f)

Yield after recrystallization from toluene: 358 mg (12%) pale yellow crystals, which melt at 150 °C to the smectic phase. EIMS: m/z (%) 596 (100) [M<sup>++</sup>], 456 (8), 316 (6), 57 (5). Anal. Calcd for C<sub>40</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub> (596.9): C 80.49, H 9.46, N 4.69; found: C 80.25, H 9.31, N 4.78.

#### 4.3.7. (E,E)-3,6-Bis[2-(4-dodecyloxyphenyl)vinyl]pyridazine (3g)

Yield after recrystallization from CHCl<sub>3</sub>: 2.25 g (69%) pale yellow crystals, which melt at 139 °C to the smectic phase. EIMS: m/z (%) 652 (100) [M<sup>++</sup>], 484 (25), 316 (13), 85 (11), 71 (17), 57 (46). Anal. Calcd for C<sub>44</sub>H<sub>64</sub>N<sub>2</sub>O<sub>2</sub> (653.0): C 80.93, H 9.89, N 4.29; found: C 80.84, H 10.04, N 4.28.

#### 4.3.8. (E,E)-3,6-Bis[2-(4-octadecyloxyphenyl)vinyl]pyridazine (3h)

Yield after recrystallization from CHCl<sub>3</sub>: 900 mg (22%) pale yellow crystals, which melt at 135 °C to the smectic phase. FD MS: m/z (%) 821 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>56</sub>H<sub>88</sub>N<sub>2</sub>O<sub>2</sub> (821.3): C 81.89, H 10.80, N 3.41; found: C 81.79, H 10.78, N 3.58.

## 4.3.9. rac-(E,E)-3,6-Bis{2-[4-(1-methylheptyloxy)phenyl]vinyl}-pyridazine (**3i**)

The washed residue was purified by column chromatography  $(3 \times 40 \text{ cm SiO}_2, \text{ toluene/ethyl acetate 8:2})$ . Recrystallization from *n*-hexane yielded 244 mg (9%) pale yellow crystals, which melt at 124 °C to the smectic phase. EIMS: m/z (%) 540 (100) [M<sup>++</sup>], 427 (38), 316 (58), 57 (40), 43 (57). Anal. Calcd for C<sub>36</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub> (540.8): C 79.96, H 8.95, N 5.18; found: C 79.92, H 9.04, N 5.31.

# 4.3.10. (S,S)-(E,E)-3,6-Bis{2-[4-(1-methylheptyloxy)phenyl]vinyl}-pyridazine (3j)

The purification of the crude product was performed as described for **3i**. Yield and spectroscopic data correspond to **3i**, however, the pale yellow crystals of **3j** melt already at 104 °C to the smectic phase.

#### 4.3.11. (E,E)-3,6-Bis[2-(3,4-dihexyloxyphenyl)vinyl]pyridazine (**3k**)

Yield after recrystallization from toluene, to which petroleum ether (bp 40–70 °C) was added till the hot solution became turbid: 1.68 g (49%) yellow crystals, which melt at 128 °C to the isotropic phase. EIMS: m/z (%) 684 (100) [M<sup>++</sup>], 600 (22). Anal. Calcd for C<sub>44</sub>H<sub>64</sub>N<sub>2</sub>O<sub>4</sub> (685.0): C 77.15, H 9.42, N 4.09; found: C 77.01, H 9.38, N 4.17.

#### 4.3.12. (E,E)-3,6-Bis[2-(3,4-didodecyloxyphenyl)vinyl]pyridazine (**3l**)

Yield after recrystallization from CHCl<sub>3</sub>: 3.21 g (63%) yellow crystals, which melt at 121 °C to the smectic phase. FD MS: m/z (%) 1021 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>68</sub>H<sub>112</sub>N<sub>2</sub>O<sub>4</sub> (1021.7): C 79.94, H 11.06, N 2.74; found: C 80.26, H 11.07, N 2.71.

#### 4.3.13. (E,E)-3,6-Bis[2-(3,4-dihexadecyloxyphenyl)vinyl]pyridazine (**3m**)

Yield after recrystallization from CHCl<sub>3</sub>: 3.73 g (60%) yellow crystals, which melt at 118 °C to the smectic phase. FD MS: m/z (%) 1245 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>84</sub>H<sub>144</sub>N<sub>2</sub>O<sub>4</sub> (1246.1): C 80.97, H 11.65, N 2.25; found: C 81.20, H 11.57, N 2.41.

#### 4.3.14. (*E*,*E*)-3,6-*B*is[2-(4-dodecyloxy-3-methoxyphenyl)vinyl]pyridazine (**3n**)

Yield after recrystallization from toluene: 570 mg (16%) yellow crystals, which melt at 61 °C to the smectic phase. FD MS: m/z (%) 712 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>46</sub>H<sub>68</sub>N<sub>2</sub>O<sub>4</sub> (713.1): C 77.48, H 9.31, N 3.93; found: C 77.21, H 9.38, N 4.18.

#### 4.3.15. (*E*,*E*)-3,6-*B*is[2-(3,4,5-trimethoxyphenyl)vinyl]pyridazine (**30**)

The crude reaction product was dried and extracted with *n*-hexane in a Soxhlet apparatus. After evaporation of the solvent, the residue was purified by column chromatography ( $30 \times 3$  cm SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>-CO-CH<sub>3</sub> 85:15). A yellow solid (185 mg, 8%) was obtained, which decomposed slowly on heating above 170 °C. FD MS: *m*/*z* (%) 465 (100) [M+H<sup>+</sup>]. Anal. Calcd for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>

(464.5): C 67.23, H 6.08, N 6.03; found: C 66.91, H 6.27, N 6.34. Application of the corresponding aldehyde with a CDO group led to an analogous result. The deuterated compound was used to control the assignment of the <sup>1</sup>H and <sup>13</sup>C NMR signals of the olefinic double bonds.

#### 4.3.16. (*E*,*E*)-3,6-*B*is[2-(3,4,5-*trihexyloxyphenyl*)vinvllpvridazine (**3p**)

Yield after recrystallization from isopropanol: 1.55 g (35%) yellow, highly viscous smectic phase, which shows a clearing point to the isotropic phase at 77 °C. Cooling down to -70 °C, does not lead to a crystalline phase. FD MS: *m/z* (%) 885 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>56</sub>H<sub>88</sub>N<sub>2</sub>O<sub>6</sub> (885.3): C 75.97, H 10.02, N 3.16; found: C 76.05, H 10.03, N 3.39.

#### 4.3.17. (E,E)-3,6-Bis[2-(3,4,5-tridecyloxyphenyl)vinyl]pyridazine (**3q**)

The crude reaction product was purified by column chromatography ( $40 \times 3$  cm SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) and subsequent crystallization from ethanol. Yield: 0.61 g (10%) yellow, smectic phase, which does not crystallize on cooling down to -70 °C. The onset temperature in the DSC for the transition to the isotropic phase is 96 °C. FD MS: *m/z* (%) 1121 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>80</sub>H<sub>136</sub>N<sub>2</sub>O<sub>6</sub> (1222.0): C 78.63, H 11.22, N 2.29; found: C 78.40, H 11.62, N 2.27.

#### 4.3.18. (E,E)-3,6-Bis[2-(3,4,5-tridodecyloxyphenyl)vinyl]pyridazine (**3r**)

The crude reaction product was purified by column chromatography ( $60 \times 3 \text{ cm SiO}_2$ , CH<sub>2</sub>Cl<sub>2</sub>) and recrystallized from isopropanol. Yield: 1.39 g (20%) yellow smectic phase, which shows the clearing point at 84 °C (onset temperature in the DSC). Cooling leads to crystallization and a phase transition to the smectic phase at 14 °C. FD MS: m/z (%) 1390 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>92</sub>H<sub>160</sub>N<sub>2</sub>O<sub>6</sub> (1390.3): C 79.48, H 11.60, N 2.01; found: C 79.49, H 11.56, N 2.06.

#### 4.3.19. (E,E)-3,6-Bis[2-(4-dodecyloxy-3,5-dimethoxyphenyl)vinyl]pyridazine (**3s**)

Yield after recrystallization from petrol ether (bp 40–70 °C): 0.46 g (12%) yellow crystals, which melt at 11 °C to the smectic phase. FD MS: m/z (%) 772 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>48</sub>H<sub>72</sub>N<sub>2</sub>O<sub>6</sub> (773.1): C 74.57, H 9.39, N 3.62; found: C 74.29, H 9.09, N 3.82.

#### 4.3.20. (E,E)-3,6-Bis[2-(3,4-didodecyloxy-5-methoxyphenyl)-

#### vinyl]pyridazine (**3t**)

Yield after recrystallization from *n*-hexane: 650 mg (12%) yellow crystals, which melt at 30 °C to the smectic phase. FD MS: m/z (%) 1081 (100) [M<sup>++</sup>]. Anal. Calcd for C<sub>70</sub>H<sub>116</sub>N<sub>2</sub>O<sub>6</sub> (1081.7): C 77.73, H 10.81, N 2.59; found: C 77.43, H 10.87, N 2.95.

#### 4.4. Irradiation experiments

Even in the daylight, solutions of **3** proved to be susceptible to photoisomerization reactions. The study of the photochemistry of (*E*,*E*)-**3d** was performed with a  $2 \times 10^{-4}$  M solution in oxygen-free benzene (17.4 mg in 180 mL) at 30 °C. Light source was a 450 W Hanovia medium pressure lamp equipped with a Pyrex filter ( $\lambda \ge 290$  nm). The emission range of the lamp reached from this filter limit to the visible region, so that the whole long-wavelength absorption of **3d** ( $\lambda_{max}=372$  nm,  $\varepsilon_{max}=52,000$  L mol<sup>-1</sup> cm<sup>-1</sup>) was covered. Magnetic stirring or a slow stream of oxygen-free N<sub>2</sub> served for the mixing of the solution. In order to follow the progress of the reaction, probes for the UV/vis spectroscopy were taken. As soon as the photostationary state was obtained, the solvent was evaporated and the residue dissolved in C<sub>6</sub>D<sub>6</sub>. Repeated <sup>1</sup>H NMR

measurements were used for the quantification of the (E,E)-**3d**/(E,Z)-**3d** ratio, which amounted to 54:46 under the conditions used.

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