Liquid-Crystalline Properties of Unsaturated Piperazine-2,5-dione Derivatives

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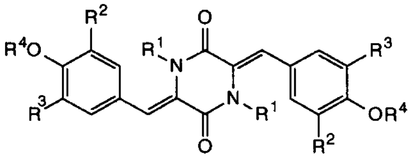
The synthesis, characterization, and mesomorphic properties of a new type of liquid-crystalline compounds, (3*Z*,6*Z*)-3,6-bis(3,4-dialkoxybenzylidene)piperazine-2,5-diones are reported. These compounds were derived from unsaturated piperazine-2,5-dione as the core group, and were prepared by condensation reactions of 1,4-diacetylpiperazine-2,5-dione and 3,4-dialkoxybenzaldehydes. The products were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, and elemental analysis, and the phase behavior of these compounds was characterized and studied by differential scanning calorimetry (DSC) and polarization microscopy. The results indicate that these rod-like compounds exhibit smectic C (S_c) phases. However, for the derivatives with two flexible alkoxy side chains, highly ordered smectic G (S_G) phases were also formed and confirmed by X-ray powder diffraction. The liquid crystallinity of these molecules was attributed to the presence of intermolecular hydrogen bonds involving the NH groups of the heterocyclic rings. The correlation of phase behavior and molecular shape is also discussed.

1. Introduction. – Organic structures that exhibit calamitic liquid-crystalline properties often contain a long rigid core which consists of fused delocalized ring systems [1]. In recent years, there has been considerable interest in materials based on heterocyclic molecules [2], especially structures incorporating heterocyclic five-membered rings such as thiophenes, pyrazoles, or isoxazoles, due to their diverse structural features and remarkable mesomorphic properties. Structures incorporating five-membered rings, however, are generally considered less suitable than six-membered rings for the formation of mesogenic phases, since they tend to deviate from linearity. Furthermore, the presence of lone-pair electrons in these heterocyclic rings introduces a transverse dipole moment, often resulting in a change of dielectric anisotropy [3]. It is well understood that mesomorphic behavior is determined and/or controlled by a combination of many structural features, including molecular shape, and rigidity, side-chain density, *etc.* Rod-shaped molecules with appropriate length/width ratios often experience anisotropic intermolecular forces and thus generally assemble to form smectic (S) or nematic (N) mesophases.

In this work, a new type of rod-like compounds (*cf.* **1**–**3**), in which the unsaturated structure of piperazine-2,5-dione was used as part of the rigid core, were prepared and their mesomorphic properties studied. All studies of piperazine-2,5-dione (also termed cyclodipeptide) derivatives in the literature have exclusively focused on the chemical and catalytic [4a], or biological [4b] activities; a study of the role of piperazine-2,5-dione derivatives as the core group in molecular organization has not yet appeared. A few interesting aspects deserve special attention: *1*) H-bonding by the NH groups, *2*) stacking interactions due to weak π-π attractive forces between the aromatic and heterocyclic rings, and *3*) hydrophobic interactions of aliphatic side chains. Structurally, the six-membered ring of piperazine-2,5-dione derivatives can adopt either a flat conformation or a slightly puckered boat form depending on substituents, and intermolecular H-bonding can give rise to the formation of a relatively rigid molecular framework. The role of H-bonding by the amide functional group of the piperazine-2,5-dione derivatives was probed with compound **4**e.



1 $R^1 = R^2 = R^3 = H$, $R^4 = Me(CH_2)_nCH_2$
2 $R^1 = R^2 = H$, $R^3 = Me(CH_2)_nCH_2O$, $R^4 = Me(CH_2)_nCH_2$
3 $R^1 = H$, $R^2 = R^3 = Me(CH_2)_nCH_2O$, $R^4 = Me(CH_2)_nCH_2$
4 $R^1 = Me$, $R^2 = H$, $R^3 = Me(CH_2)_nCH_2O$, $R^4 = Me(CH_2)_nCH_2$

a $n = 3$ **e** $n = 10$
b $n = 4$ **f** $n = 12$
c $n = 6$ **g** $n = 14$
d $n = 8$

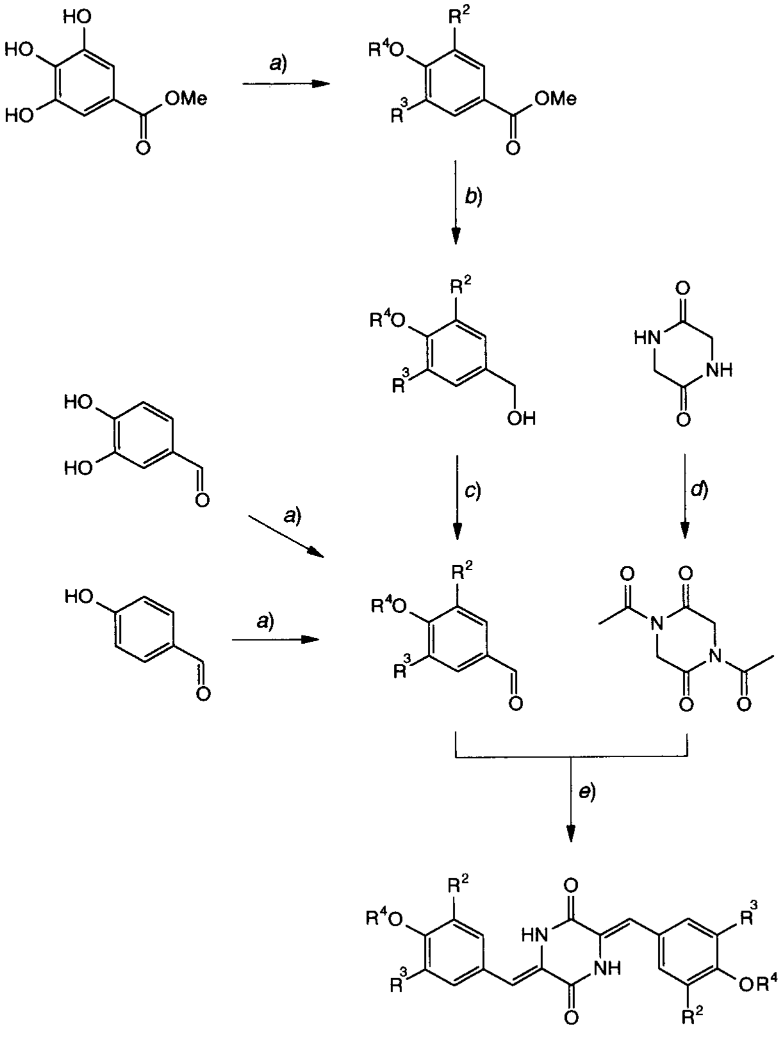
2. Results and Discussion. – 2.1. *Synthesis.* The synthetic procedures for these compounds are given in *Scheme 1.* The preparations of 4-alkoxybenzaldehydes, 3,4-dialkoxybenzaldehydes, methyl 3,4,5-trialkoxybenzoates, and 3,4,5,-trialkoxybenzoic acids were according to the literature [5]. The 3,4,5-trialkoxybenzaldehydes were prepared by the reaction of 3,4,5-trialkoxybenzyl alcohols with pyridinium chlorochromate (PCC) in CH_2Cl_2 at room temperature. The $C(3)H_2$ and $C(6)H_2$ groups of piperazine-2,5-dione are known to undergo facile condensation with aromatic aldehydes to form symmetric dibenzylidene derivatives. The 3,6-bis(3,4-dialkoxybenzylidene)piperazine-2,5-diones were thus obtained by condensation of 1,4-diacetylpiperazine-2,5-dione with appropriate benzaldehydes in the presence of a base (*e.g.*, Cs_2CO_3), and were isolated as light yellow needles.

The *N*-methylated compound **4e** was prepared by substitution of **2e** with MeI in THF and NaH as base at room temperature (*Scheme 2*)

These derivatives were characterized by ^1H- and ^{13}C-NMR spectroscopy. The NMR data revealed that these compounds are in the (all-*Z*)-configuration, and that the vinylic proton is generally deshielded by *ca.* 0.65 ppm in the (*Z*)-isomer compared to the (*E*)-isomer [6]. The ^1H-NMR data of (3*Z*,6*Z*)-3,6-bis(4-dodecyloxybenzylidene)piperazine-2,5-dione (**2e**, $n = 10$, where n corresponds to the number of CH_2 groups in the chain) in $CDCl_3$ showed two characteristic peaks at 6.93 and 8.00 ppm, which were assigned to the olefinic methine and NH protons. The signal of NH often appeared at higher magnetic field. In the IR spectrum the C–O stretching bands occurred at 1670–1690 cm^{-1} and the N–H stretching frequency at 3180–3195 cm^{-1} [7].

2.2. *Mesomorphic Properties.* The liquid crystalline behavior of these compounds was studied by differential scanning calorimetry (DSC) and polarization microscopy. The phase transitions for compounds **1**–**3** are summarized in *Table 1.* The results indicate that the phase of these compounds is quite sensitive to the number of flexible alkoxy side chains.

Scheme 1



1–3

a) RBr (1.0–3.0 equiv.), K_2CO_3 (3.0–7.0 equiv.), KI (cat.), at reflux in dry acetone 18–72 h; 72–96%. *b*) $LiAlH_4$ (1.1 equiv.), stirred at r.t. in dry THF 1 h, then refluxed 30 min; 77–93%. *c*) PCC (1.1 equiv.), stirred in dry CH_2Cl_2 8 h; 80–91%. *d*) Ac_2O (2.0M), stirred at 130° 12 h; 75–82%. *e*) Cs_2CO_3 (2.1 equiv.), stirred in DMF/toluene 1:1 at 80° 7 h; 65–72%.

2.2.1. *Side-Chain Length.* All (3*Z*,6*Z*)-3,6-bis(3,4-dialkoxybenzylidene)piperazine-2,5-diones **2** exhibited a tilted structure in the enantiotropic smectic phase. For the compounds **2** having shorter C-chains (*e.g.*, **2a** and **b**, *n* = 3, 4, resp.), only the crystal-to-isotropic transition was observed. However, an enantiotropic phase for compounds with longer C-chains (**2e**–**g**, *n* = 6, 8, 10, 12, 14, resp.) was identified as smectic C based

Scheme 2

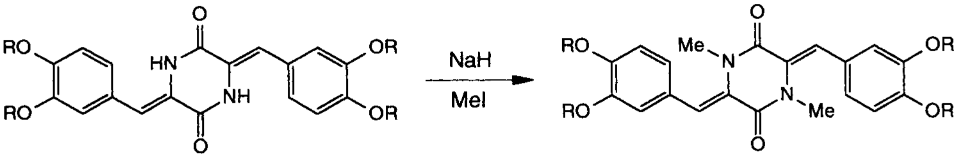


Table 1. *Phase Behavior of* **1**–**3**. Transition temperatures [°] and enthalpies (in parenthesis, [kJ/mol]) determined by DSC at a scan rate of 10.0°/min.

	n[a])	Crystal Phases[b])						
1e	10	K_1	$\underset{162.3(3.21)}{\overset{189.3(5.52)}{\rightleftharpoons}}$	K_2	$\underset{182.4(4.98)}{\overset{195.3(2.49)}{\rightleftharpoons}}$	S_G	$\underset{220.7(18.6)}{\overset{225.5(21.0)}{\rightleftharpoons}}$	I
1f	12	K_1	$\underset{181.7(4.60)}{\overset{199.2(5.54)}{\rightleftharpoons}}$	K_2	$\underset{207.7(1.04)}{\overset{226.0(1.04)}{\rightleftharpoons}}$	S_G	$\underset{239.5(23.0)}{\overset{243.2(24.3)}{\rightleftharpoons}}$	I
1g	14	K_1	$\underset{128.6(7.45)}{\overset{131.1(8.61}{\rightleftharpoons}}$	K_2	$\underset{146.2(3.07)}{\overset{188.0(3.60)}{\rightleftharpoons}}$	S_G	$\underset{221.3(28.1)}{\overset{225.0(29.5)}{\rightleftharpoons}}$	I
2a	3					K	$\underset{169.7(38.3)}{\overset{181.0(54.3)}{\rightleftharpoons}}$	I
2b	4					K	$\underset{144.6(38.4)}{\overset{163.7(43.9)}{\rightleftharpoons}}$	I
2c	6			K	$\underset{130.0(1.74)}{\overset{132.1(3.72)}{\rightleftharpoons}}$	S_C	$\underset{145.8(35.0)}{\overset{151.0(36.4)}{\rightleftharpoons}}$	I
2d	8			K	$\underset{125.3(2.54)}{\overset{131.8(4.18)}{\rightleftharpoons}}$	S_C	$\underset{145.7(35.4)}{\overset{150.3(36.4)}{\rightleftharpoons}}$	I
2e	10			K	$\underset{75.8(28.9)}{\overset{104.5(38.7)}{\rightleftharpoons}}$	S_C	$\underset{137.3(19.5)}{\overset{149.0(20.1)}{\rightleftharpoons}}$	I
2f	12			K	$\underset{76.7(17.4)}{\overset{102.0(16.9)}{\rightleftharpoons}}$	S_C	$\underset{143.9(25.6)}{\overset{145.2(26.2)}{\rightleftharpoons}}$	I
2g	14			K	$\underset{88.6(39.6)}{\overset{108.0(34.2)}{\rightleftharpoons}}$	S_C	$\underset{136.9(29.7)}{\overset{141.8(30.2)}{\rightleftharpoons}}$	I
3e	10					K	$\underset{39.5(1.18)}{\overset{40.3(2.06)}{\rightleftharpoons}}$	I

[a]) n = the number of CH_2 groups in the alkoxy chain. [b]) K, K_1, K_2 = Crystal phases; S_G = smectic G phase, S_C = smectic C phase; I = isotropic.

on the observation of focal conic textures (see *Fig.*). Polarization microscopy of a thin layer of sample pressed between two glass plates revealed the formation of a focal-conic texture on very slow cooling from the isotropic. DSC Data showed that the transitions of crystal-to-smectic were observed over a temperature range of 102.0–132.1°, with transition enthalpies ranging from 3.72–38.7 kJ/mol; the isotropic points were all in the range of 151.0–141.8°, with enthalpies of 36.4–20.1 kJ/mol. The temperature range of the mesophase was 19.0–43.2°. The transition temperatures were slightly dependent on the length of the side chains: increasing the C-number of the side chains slightly lowered the clearing temperature. This trend is attributed to the larger dispersive forces of the longer alkoxy chains. This smectic C phase was also confirmed by X-ray powder diffraction. For example, compound **2d** ($n = 8$) at 130° exhibited only a sharp reflection at 44.53 Å in the small-angle region, indicating a diordered arrangement of layers. A more diffuse peak at 4.58 Å, related to the alkoxy chains, was also observed.

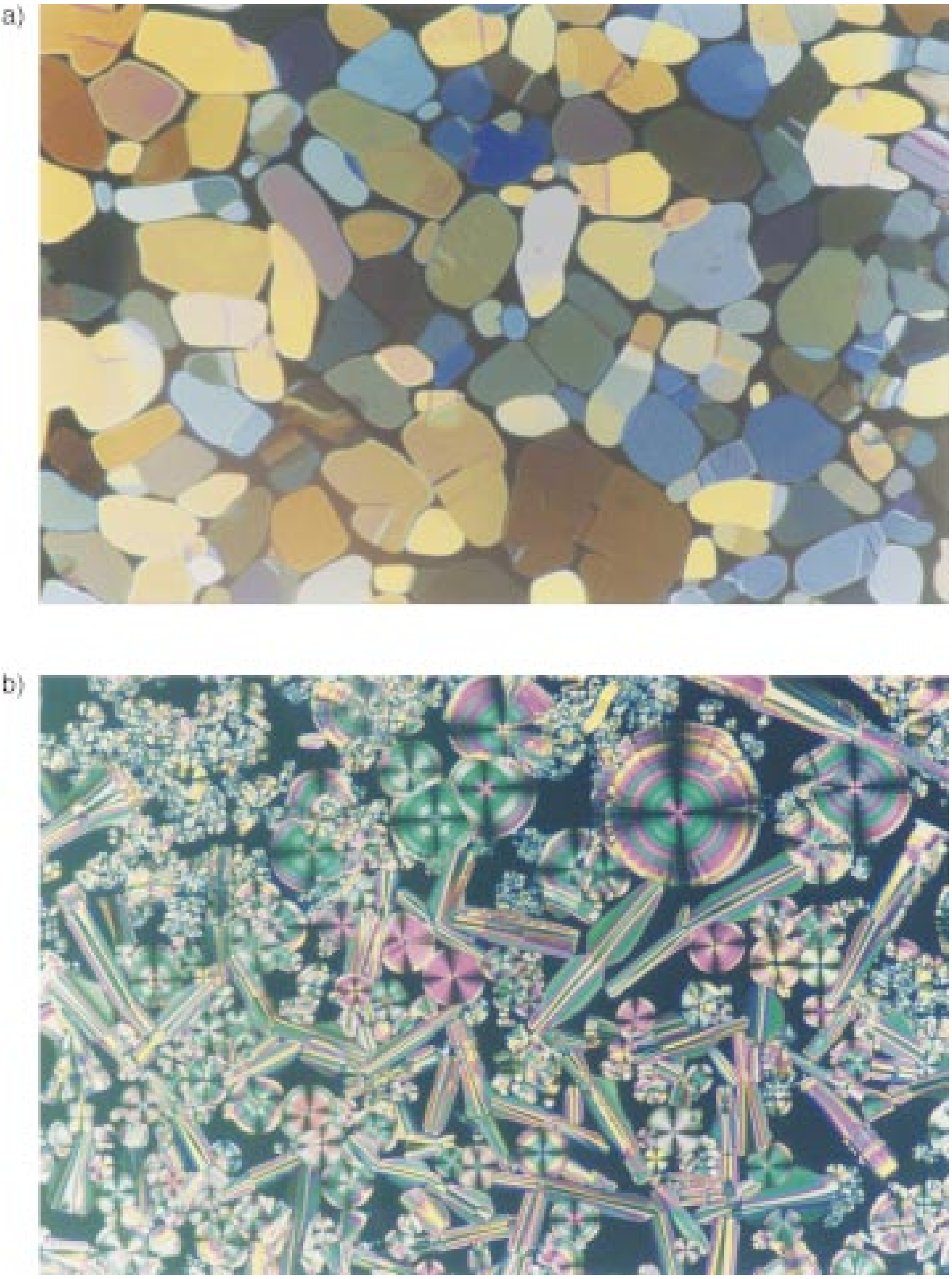


Figure. *Optical textures observed by polarization microscopy for* a) **1e** (210°) *and* b) **2e** (125°). Magnification 100 ×.

2.2.2. *Hydrogen Bonding*. To probe the contribution of amide H-bonding to the intermolecular forces in these layered structures, (3*Z*,6*Z*)-3,6-bis(3′,4′-didodecyloxybenzylidene)-1,4-dimethylpiperazine-2,5-dione (**4e**) was prepared and studied. Substitution of the two amide H-atom of the piperazinedione ring by a tetrahedral Me group decreases the intermolecular force between layers through disruption of the H-bonding network and increased distance between layers. DSC Data indicated that the mesomorphism was destroyed, and that this compound undergoes a crystal-to-isotropic transition at 60.0°.

2.2.3. *Side-Chain Density*. The dependence of mesophase formation on the numbers of side chains (*i.e.*, side-chain density) was also studied. Various (3*Z*,6*Z*)-3,6-bis(4-alkoxybenzylidene)piperazine-2,5-diones (**1e**–**g**, $n = 10$, 12, and 14, resp.) and (3*Z*,6*Z*)-3,6-bis(3, 4, 5-trialkoxybenzylidene)piperazine-2,5-diones (**3e**, $n = 10$) were also prepared and their properties investigated. An increase in the number of side chains slightly altered the molecular shape from more rod-like in compounds **1** to more lath-like in compounds **3**. Compounds **1** exhibited similar tilted smectic phases which were tentatively assigned as smectic G on the basis of observed mosaic textures (*Fig.*). The clearing temperatures for compounds **1**, ranging from 225.0–243.2° in DSC experiments, which were much higher than those for compounds **2**, indicate a highly ordered molecular arrangement. However, this mesophase of highly ordered structures exhibited liquid-like behavior, and the isotropic-to-mesophase transition in cooling cycles exhibited no supercooling. The X-ray powder data also confirmed this highly ordered state. The diffraction pattern at 150° for compound **1f** ($n = 12$) appeared at 40.46 Å, 20.87 Å, 15.33 Å, and 7.52 Å in the small-angle region, and at 4.81 Å, 4.57 Å, 4.42 Å, 4.25 Å, 3.83 Å, and 3.42 Å in the wide-angle region. Finally, the broader compounds **3** formed only the crystalline phase.

3. Conclusions. – The formation of liquid-crystalline phases directed by weak H-bonding was demonstrated in derivatives of (3*Z*,6*Z*)-3,6-bis(3,4-dialkoxybenzylidene)piperazine-2,5-diones. The overall molecular shapes for the piperazine-2,5-dione-based derivatives are rod-like or lath-like depending on the number of flexible side chains attached to the benzylidene ring. The relatively rigid structure of the piperazine-2,5-dione as core group increased the interactive forces between the layers in the smectic arrangement.

Experimental Part

General. All chemicals and solvents were reagent-grade from *Aldrich Chemical Co.* NMR-Spectra: *Bruker DRS-200*; δ in ppm and J in Hz. DSC Thermography was carried out on a *Perkin-Elmer DSC-7* calibrated with a pure In sample. All thermal phase behavior was determined with a scan rate of 10.0°/min. Polarization microscopy was carried out on *Nikkon MICROPHOT-FXA* with a *Mettler FP90/FP82 HT* hot-stage system. Elemental analyses for C, H, and N were conducted on a *Heraeus CHN-O* rapid elemental analyzer and the results are given in *Table 2*.

1,4-Diacetylpiperazine-2,5-dione. Piperazine-2,5-dione (1.05 g, 9.20 mmol) and Ac_2O (4.60 ml) were stirred at 130° for 12 h. The soln. was concentrated under reduced pressure, and the solids were redissolved in 100 ml of AcOEt. The soln. was extracted with $NaHCO_3$ (5% soln.), dil. HCl (5%), and brine. The org. layer was dried (Na_2SO_4) and concentrated to give brown solids. Pale yellow crystals were obtained after recrystallization from AcOEt/hexane. Yield 86%. M.p. 151.6°. ^{1}H-NMR ($CDCl_3$): 2.54 (*s*, 2 Me); 4.55 (*s*, 2 CH_2). ^{13}C-NMR ($CDCl_3$): 26.65 (Me); 47.13 (C(1), C(4)); 165.82 (CO); 170.68 (C(2), C(5)).

Table 2. *Elemental-Analysis Data* [%] *for* **1**–**4** (calculated values in parentheses)

Compound	n[a])	C	H
1e	10	76.24 (76.55)	10.00 (9.48)
1f	12	77.42 (77.27)	9.19 (9.87)
1g	14	77.69 (77.87)	10.18 (10.19)
2b	4	73.09 (73.01)	9.02 (9.04)
2d	8	75.91 (76.10)	10.33 (10.35)
2e	10	77.11 (77.14)	10.71 (10.79)
2f	12	77.69 (77.98)	11.15 (11.14)
2g	14	78.77 (78.66)	11.30 (11.43)
3e	10	77.28 (77.42)	11.52 (11.41)
4e	10	77.19 (77.37)	10.95 (10.88)

[a]) n = Number of CH_2 groups in alkoxy chain.

4-Dodecyloxybenzaldehyde. Yield: 87%. White solid. M.p. 38.6°. ^1H-NMR ($CDCl_3$): 0.85 (t, $J = 6.10$, Me); 1.13–1.47 (m, 9 CH_2); 1.71–1.85 (m, 2 CH_2); 4.01 (t, $J = 6.40$, CH_2O); 6.96 (d, $J = 8.40$, 2 arom. H); 7.79 (d, $J = 9.01$, 2 arom. H); 9.85 (s, CHO). ^{13}C-NMR ($CDCl_3$): 14.07; 22.65; 25.93; 29.03; 29.31; 29.63; 31.89; 68.40; 114.72; 129.73; 131.94; 164.25; 190.73.

3,4-Didodecyloxybenzaldehyde. Yield: 83%. White crystals. M.p. 73.7°. ^1H-NMR ($CDCl_3$): 0.79 (t, $J = 6.79$, 2 Me); 1.18–1.38 (m, 19 CH_2); 1.68–1.75 (m, 2 CH_2); 3.97 (q, $J = 6.5$, 2 CH_2O); 6.78 (d, $J = 17.9$, 1 arom. H); 7.33 (s, 1 arom. H); 7.37 (d, $J = 12.0$, 1 arom. H); 9.73 (s, CHO). ^{13}C-NMR ($CDCl_3$): 14.01; 22.61; 25.92; 28.94; 29.02; 29.30; 29.55; 31.86; 69.04; 110.97 (C(6)); 111.72 (C(2)); 126.43 (C(5)); 129.85 (C(1)); 149.41 (C(4)); 154.63 (C(3)); 190.72 (CO).

3,4,5-Tridodecyloxybenzyl Alcohol. Methyl 3,4,5-tridodecyloxybenzoate (10.0 g, 0.0145 mol) in 100 ml of dry THF was added dropwise to a suspension of $LiAlH_4$ (0.61 g, 0.0161 mol) in THF soln. at ice-bath temp. The mixture was stirred at r.t. for 2 h, and then refluxed for 30 min. HCl (1.0M) was added to neutralize the soln., and the soln. was extracted twice with $CHCl_3$. The combined $CHCl_3$ phases were evaporated to give pale yellow solids. Recrystallization from acetone/MeOH gave white solids. Yield: 90%. ^1H-NMR ($CDCl_3$): 0.86 (t, 3 Me); 1.24–1.80 (m, 30 CH_2); 3.94 (t, 3 CH_2O); 4.55 (s, CH_2OH); 6.52 (d, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 14.10; 22.68; 26.13; 29.40; 29.49; 29.67; 29.78; 31.99; 32.01; 65.28; 68.88; 73.26; 114.97; 135.94; 137.67; 153.11.

3,4,5-Tridodecyloxybenzaldehyde. 3,4,5-Tridodecyloxybenzyl alcohol (5.00 g, 0.0075 mol) in dry CH_2Cl_2 (100 ml) was slowly added to a soln. of pyridinium chlorochromate (1.80 g, 0.0084 mmol) in CH_2Cl_2 (20 ml). The soln. was stirred for 4 h., filtered through *Celite*, and the solvent was removed under reduced pressure. The residue was purified by chromatography (silica gel; hexane/AcOEt, 5:1). White solids were obtained after recrystallization from CH_2Cl_2/MeOH. Yield: 75%. M.p. 49.8°. ^1H-NMR ($CDCl_3$): 0.85 (t, $J = 6.38$, 3 Me); 1.24–1.49 (m, 27 CH_2); 1.66-1.83 (m, 3 CH_2); 4.02 (q, $J = 6.00$, 3 CH_2O); 7.05 (s, 2 arom. H); 9.80 (s, CHO). ^{13}C-NMR ($CDCl_3$): 14.08; 22.67; 26.04; 29.23; 29.35; 29.67; 30.32; 31.91; 69.21; 73.61; 107.82; 131.42; 143.81; 153.50; 191.26.

(3Z,6Z)-3,4-Bis(4-dodecyloxybenzylidene)piperazine-2,5-dione (**1e**). Yield: 72%. M.p. 225.5°. IR (KBr): 3218, 2922, 2847, 1684, 1626, 1603, 1514, 1472, 1412, 1356, 1250, 1180, 796. ^1H-NMR ($CDCl_3$): 0.88 (t, $J = 6.13$, 2 Me); 1.18–1.38 (m, 18 CH_2); 1.72–1.83 (m, 2 CH_2); 4.00 (t, $J = 6.50$, 2 CH_2O); 6.93 (s, 2 CH=C); 6.95 (d, $J = 7.71$, 4 arom. H); 7.31 (d, $J = 8.34$, 4 arom. H); 8.00 (s, 2 NH). ^{13}C-NMR ($CDCl_3$): 13.88; 22.65; 26.09; 29.33; 29.66; 31.94; 68.57; 115.87; 116.32; 124.63; 125.32; 130.03; 157.32; 159.94. Anal. calc. for $C_{42}H_{62}N_2O_4$: C 76.55, H 9.48, N 4.25; found: C 75.52, H 9.54, N 4.21.

(3Z,6Z)-3,6-Bis(3,4-didodecyloxybenzylidene)piperazine-2,5-dione (**2e**). 1,4-Diacetylpiperazine-2,5-dione (0.70 mg, 3.51 mmol) and 3,4-didodecyloxybenzaldehyde (3.51 g, 3.51 mmol) were mixed in 25.0 ml of DMF/toluene 1:1, $CeCO_3$ (2.41 mg, 7.38 mmol) was added under N_2, and the mixture was stirred at 80° for 7 h. The soln. was concentrated to give yellow solids, which were washed with AcOEt several times until the filtrate was completely colorless. Pale yellow solids were obtained after recrystalliztion from hot THF. Yield: 65%. M.p. 148.0°. IR (neat): 3171, 2922, 2847, 1682, 1634, 1595, 1518, 1464, 1408, 1352, 1335, 1263, 1234, 1130, 1024, 783, 723. ^1H-NMR ($CDCl_3$): 0.86 (t, $J = 6.20$, 4 Me); 1.24–1.56 (m, 36 CH_2); 1.77–1.80 (m, 4 CH_2); 3.99 (q, $J = 6.59$, 4 CH_2O); 6.84 (s, 2 CH=C); 6.87–6.98 (m, 6 arom. H); 8.13 (s, 2 NH). ^{13}C-NMR ($CDCl_3$): 13.92; 22.65; 26.13;

26.35; 29.35; 29.45; 29.65; 31.95; 69.83; 70.10; 115.18; 115.42; 116.54; 121.45; 124.98; 125.98; 150.30; 150.57; 157.22. Anal. calc. for $C_{66}H_{110}N_2O_6$: C 77.14, H 10.79, N 2.73; found: C 77.11, H 10.71, N 3.37.

(3Z,6Z)-3,6-Bis(3,4,5-tridodecyloxybenzylidene)piperazine-2,5-dione (**3e**). Yield: 71%. M.p. 89.6°. IR (KBr): 3177, 2928, 2845, 1678, 1628, 1582, 1473, 1448, 1404, 1333, 1240, 1120, 721. ^{1}H-NMR ($CDCl_3$): 0.87 (*t*, *J* = 6.35, 6 Me); 1.17 – 1.46 (*m*, 54 CH_2); 1.68 – 1.86 (*m*, 6 CH_2); 3.94 – 4.02 (*m*, 6 CH_2O); 6.64 (*s*, 4 arom. H); 6.90 (*s*, 2 CH=C); 8.08 (*s*, 2 NH). ^{13}C-NMR ($CDCl_3$): 14.09; 22.68; 26.09; 29.37; 29.64; 30.32; 31.92; 69.39; 73.62; 106.92; 117.16; 125.08; 127.55; 139.06; 153.93; 156.95. Anal. calc. for $C_{90}H_{158}N_{208}$: C 77.42, H 11.41, N 2.01; found: C 76.28, H 11.52, N 1.90.

(3Z,6Z)-3,6-Bis(3,4-didodecyloxybenzylidene)-N,N-*dimethylpiperazine-2,5-dione* (**4e**). A mixture of **2e** (508 mg, mmol) and MeI (0.078 ml, mmol) was dissolved in THF (5.0 ml), 60% NaH (50.4 mg, mmol) was added, and the mixture was stirred at r.t. for 8 h. The soln. was concentrated to dryness, and the solid was redissolved in AcOEt (10 ml). The soln. was washed with HCl (5%). The org. layer was collected and dried. Light yellow solids were obtained after recrystallization from hot THF. Yield: 83%. M.p. 60.0°. IR (KBr): 2921, 2851, 1686, 1627, 1520, 1470, 1426, 1379, 1343, 1269, 1190, 1136, 1024, 810, 756, 716. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 6.17, 4 Me); 1.26 – 1.57 (*m*, 36 CH_2); 1.79 – 1.82 (*m*, 4 CH_2); 3.02 (*s*, 2 MeN); 3.99 (*q*, *J* = 6.45, 4 CH_2O); 6.82 – 6.86 (*m*, 6 arom. H); 7.12 (*s*, 2 CH_2=C). ^{13}C-NMR ($CDCl_3$): 14.10; 22.66; 26.01; 29.35; 29.62; 31.56; 31.90; 35.23; 69.00; 69.37; 112.68; 114.90; 121.97; 123.09; 125.76; 129.95; 148.62; 149.68; 162.81. Anal. calc. for $C_{68}H_{114}N_2O_6$: C 77.37, H 10.88, N 2.65; found: C 77.11, H 10.71, N 2.62.

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