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Heterocyclic 1,3,4-oxadiazole as columnar core

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The synthesis, characterization and mesomorphic properties of a new type of liquid crystalline compound, the 2,5-bis(3,4,5-trialkoxyphenyl)-1,3,4-oxadiazoles, **3a**–**3h**, are reported. These heterocyclic compounds are derived from unsaturated 1,3,4-oxadiazole as the core group, and obtained by the condensation reaction of 3,4,5-trialkoxybenzoic acid *N*-(3,4,5-trialkoxybenzoyl)-hydrazides and phosphorus oxychloride in toluene under reflux. All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis. The mesomorphic properties of these and the related compounds **1**, **2** were characterized and studied by differential scanning calorimetry and polarizing optical microscopy. The formation of columnar mesophases was found to be dependent on the numbers of alkoxy sidechains. The compounds **3** exhibited hexagonal columnar (Col_h) phases, however compounds **1**, **2** formed crystalline phases. Compounds **3b**–**3e** with shorter carbon chains were room temperature liquid crystals. Polar induction by nitrogen and/or oxygen atoms on the heterocyclic core ring might be responsible for the formation and better observed mesomorphic properties in this type of compound.

1. Introduction

In recent years the significant interest in mesomorphic heterocyclic compounds [1] has dramatically increased due to their more diversified structural figures and distinct mesomorphic properties. Numerous unsaturated structures forming a variety of molecular shapes have been generated and found to exhibit interesting mesomorphic properties. Most of this type of compound form nematic/smectic phases, and examples exhibiting columnar phases are relatively limited. Furthermore, significant compounds have a six-membered or larger fused ring as core group, and the heteroatoms incorporated include nitrogen, oxygen or sulfur. Typical examples having such cores are the benzotrisfurans [2], pyrillium salts [3], ionic dithiolium salts [4], bispyran salts [5], tricycloquinazolines [6], phthalocyanines [7], and porphyrins [8].

Examples of disc molecules with five-membered rings are relatively rare. Whereas most discogenic cores used had a rigid and/or planar structure with a higher rotational symmetry, examples of molecules with a low symmetry and/or non-planar structure are also known. Utilization of unique heterocyclic structures [9] in which the molecular symmetry of the central core is reduced would probably lead to a lowering of melting points due to less favourable packing in the crystalline state. This lowering in melting points greatly increases the potential for practical applications.

In this work a series of heterocyclic compounds **1**–**3**, in which an unsaturated five-membered ring derived from 1,3,4-oxadiazole is utilized as the core centre, were prepared and their mesomorphic properties investigated. Several of this type of oxadiazole-based material have been studied and found to show novel properties [10]. Their physical behaviour was focused on electron-transporting or photoconducting capability for advanced electronic devices. For example, non-mesomorphic 2,5-bis-(4-naphthyl)-1,3,4-oxadiazole [10*a*] was shown to be one of the best organic electron conductors. However, examples of mesomorphic 1,3,4-oxadiazole derivatives are relatively scarce [11, 12]. 2,5-Bis(4-octadecyloxy-benzylidene-4-aminophenyl)-1,3,4-oxadizole, **7**, was reported to exhibit nematic/smectic phases [12*a*] and to possess an electron-transporting capability. 1,3,4-Oxadiazole derivatives were considered as non-linear mesogenic compounds. The effect of the shape, caused by a larger exocyclic bond angle ($\varepsilon \sim 134°$), on the formation of mesogenic behaviour remained unclear

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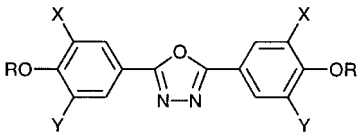
[11 *c*]. Here we report the first example derived from 1,3,4-oxadiazole that exhibits a room temperature columnar phase.



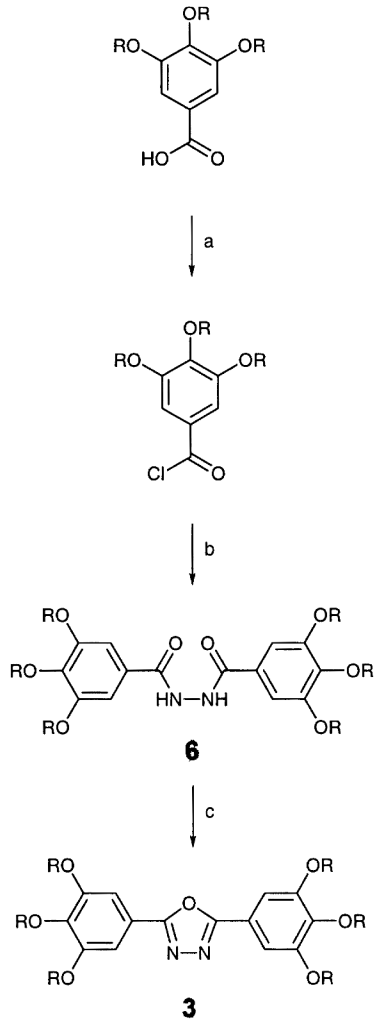
R = $(CH_2)_nH$
1 X = Y = H
2 X= OR, Y = H
3 X= Y = OR

2. Results and discussion

2.1. *Synthesis and characterization*

The general synthetic procedures for the compounds **1**–**3** are given in the scheme. The methyl 3,4,5-trialkoxybenzoate esters, 3,4,5-trialkoxybenzoic acids and 3,4,5-trialkoxybenzoic acid chlorides were prepared by literatures methods [13]. 2,4,5-Trialkoxybenzoic acid *N*-(3,4,5-trialkoxybenzoyl)hydrazides, **6**, were obtained by reaction of 3,4,5-trialkoxybenzoic acid chlorides with three equivalents of hydrazine in dried methylene chloride at room temperature. The yields were relatively high, in the range 82–91%. The final 2,5-bis(3,4,5-trialkoxyphenyl)-1,3,4-oxadiazoles **3** were prepared by condensation reactions between 3,4,5-trialkoxybenzoic acid *N*-(3,4,5-trialkoxybenzoyl)hydrazides and ten equivalents of phosphoryl chloride ($POCl_3$) in dried toluene under reflux. Replacement of $POCl_3$ by phosphorous trichloride (PCl_3) gave the same product, however, the reaction took a longer time and gave a lower reaction yield.

The compounds were isolated as white crystals or pastes depending on the carbon chain length; yields were in the range 62–71%. All derivatives were characterized by ^1H and ^{13}C NMR spectroscopy, and elemental analysis (see table 1). The ^1H NMR and ^{13}C NMR data in $CDCl_3$, for e.g. 3,4,5-trioctanoxybenzoic acid *N*-(3,4,5-trioctanoxybenzoyl)hydrazide showed one characteristic peak at δ 9.62 ppm and 171.90 ppm, respectively, and this peak was assigned to amide−H (−NH) and amide−C (−CONH). The amide −NH proton often appeared at the higher magnetic field. In the infrared spectrum the −CO stretching bands occurred at 1595–1737 cm^{-1} and the −NH stretching at 3152–3235 cm^{-1} [14].



Scheme. Reagents and reaction conditions. a: refluxing in $SOCl_2$, 1 h. b: N_2H_2 (3.0 eq), stirred in dried CH_2Cl_2, 2 h, 82–91%. c: $POCl_3$ (10.0 eq), refluxing in dried toluene, 1 h, 62–71%.

Table 1. Elemental analysis data (%) for compounds **1**–**3** with calculated values in parentheses.

Compd.	*n*	C	H	N
1	18	79.23 (79.10)	10.92 (10.89)	3.68 (3.69)
2	10	76.64 (76.55)	11.00 (10.71)	3.23 (3.31)
3h	16	79.46 (79.36)	12.31 (12.23)	1.72 (1.68)
3g	14	78.79 (78.65)	12.11 (11.99)	1.89 (1.87)
3f	12	77.61 (77.77)	11.90 (11.69)	1.97 (2.11)
3e	10	76.91 (76.63)	11.12 (11.30)	2.42 (2.42)
3d	8	74.79 (75.10)	10.94 (10.78)	2.72 (2.83)
3c	7	73.78 (74.13)	10.60 (10.44)	2.98 (3.09)
3b	6	72.63 (72.95)	10.30 (10.04)	3.17 (3.40)
3a	5	71.56 (71.51)	9.68 (9.55)	3.48 (3.79)

2.2. *Mesomorphic properties*

The similar rod-like compound, 2,5-bis(4-octadecyloxybenzylidene-4-aminophenyl)-1,3,4-oxadiazole **7** was prepared by Tsutsui [10]. This compound was found to form nematic and smectic A phases, and also possessed good electron transporting capability. To explore other

mesomorphic properties of 1,3,4-oxadiazole derivatives, compounds **1**–**3** were prepared and studied. The overall molecular shapes for these compounds is likely to be more rod-like for **1** and disc-like for **3**, and the formation of nematic/smectic or discotic phases might be expected for **1** and **3**, respectively. The mesomorphic behaviour of all the compounds was studied by thermal analysis (DSC) and polarizing optical microscopy (POM). The phase transitions and thermodynamic data for **1**–**3** are summarized in table 2. Mesophase formation was found to be dependent on the number of flexible sidechains attached to the core group. The compounds **3a**–**3h**, with a total of six sidechains, exhibited columnar phases; however all compounds **1**–**2**, with two or four sidechains, formed only crystalline phases regardless of the carbon chain length. Crystal-to-isotropic transitions at 126.3°C and 78.1°C were observed for compounds **1** and **2**, respectively. A closer comparison of molecular structures indicated that, although compound **1** is rod-like in molecular shape (similar to the reported compounds), its much shorter molecular length may lead to the lack of observed mesomorphism.

Table 2. Phase behaviour for the compounds **1**–**3**. *n* represents the number of carbons in the alkoxy chain. Cr = crystal phase; Col_{hd} = disordered hexagonal columnar phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parenthesis, kJ mol^{-1}) are determined by DSC analysis.

Compound	*n*	Phase transitions
1	18	Cr $\underset{113.8\ (131.7)}{\overset{126.3\ (128.7)}{\rightleftharpoons}}$ I
2	10	Cr $\underset{54.1\ (69.7)}{\overset{78.1\ (55.2)}{\rightleftharpoons}}$ I
3a	5	Cr $\underset{34.1\ (32.7)}{\overset{54.4\ (32.3)}{\rightleftharpoons}}$ Col_{hd} $\underset{64.0\ (3.77)}{\overset{70.6\ (2.44)}{\rightleftharpoons}}$ I
3b	6	Col_{hd} $\underset{63.7\ (5.32)}{\overset{68.3\ (5.33)}{\rightleftharpoons}}$ I
3c	7	Col_{hd} $\underset{67.2\ (5.06)}{\overset{72.1\ (5.26)}{\rightleftharpoons}}$ I
3d	8	Col_{hd} $\underset{66.1\ (5.95)}{\overset{70.5\ (5.97)}{\rightleftharpoons}}$ I
3e	10	Col_{hd} $\underset{59.3\ (5.54)}{\overset{63.8\ (5.53)}{\rightleftharpoons}}$ I
3f	12	Cr $\underset{16.0\ (49.3)}{\overset{31.9\ (36.7)}{\rightleftharpoons}}$ Col_{hd} $\underset{55.1\ (5.78)}{\overset{59.3\ (5.60)}{\rightleftharpoons}}$ I
3g	14	Cr $\underset{25.9\ (49.7)}{\overset{33.9\ (53.0)}{\rightleftharpoons}}$ Col_{hd} $\underset{53.7\ (6.19)}{\overset{58.6\ (6.38)}{\rightleftharpoons}}$ I
3h	16	Cr $\underset{41.7\ (48.5)}{\overset{51.4\ (79.5)}{\rightleftharpoons}}$ Col_{hd} $\underset{48.7\ (3.99)}{\overset{54.1\ (3.72)}{\rightleftharpoons}}$ I

Better mesomorphic properties are expected if more flexible or longer side chains are attached to the same core group of 1,3,4-oxadiazole; this modification alters the molecular shape from rod-like to more disc-like. From the thermal results (table 2) it appeared that all compounds **3** exhibit enantiotropic behaviour. All compounds **3** gave typical crystal-to-columnar and columnar-to-isotropic transitions (Cr → Col → I) by DSC analysis, as observed for discotic molecules. Mesophase-to-isotropic transitions were observed in the lower temperature range of 54.1–72.1°C on heating, the clearing temperatures decreasing with increasing length of alkoxy side chains.

Compounds **3b**–**3e** with shorter alkoxy side chains were all room temperature liquid crystals, and the crystal-to-mesophase transitions were all below room temperature. The mesophase was characteristically identified as hexagonal columnar (Col_h) based on observed optical texture. A typically pseudo focal-conic texture, as shown in the figure, with linear birefringent defects was clearly seen on slowly cooling from the isotropic liquid. This observed texture, accompanied by a large area of black homeotropic domain, is often characteristic for hexagonal columnar phases. In addition, a relatively smaller enthalpy for the columnar-to-isotropic transitions was obtained by DSC analysis, indicating that the mesophases were highly disordered.

3. Summary

A new class of mesomorphic heterocyclic molecules based on 1,3,4-oxadiazole derivatives as core group was prepared; these compounds have been demonstrated to exhibit room temperature columnar phases. Nitrogen and/or oxygen atoms, which are more polarized on the heterocyclic ring are believed to be responsible for the formation of better mesomorphic properties over all analogous-carbon five-membered ring compounds.

4. Experimental

All chemicals and solvents were reagent grades from Aldrich Chemical Co. Toluene and dichloromethane were dried by standard techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200. DSC thermographs were carried out on a Mettler DSC 821, calibrated with pure indium. All phase transitions were determined with a scan rate of 5.0°C min^{-1}. Polarizing optical microscopy was carried out on Nikkon MICROPHOT-FXA equipped with a Mettler FP90/FP82HT hot stage. Elemental analysis for carbon, hydrogen, and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyser.

The following compounds were prepared as described above.

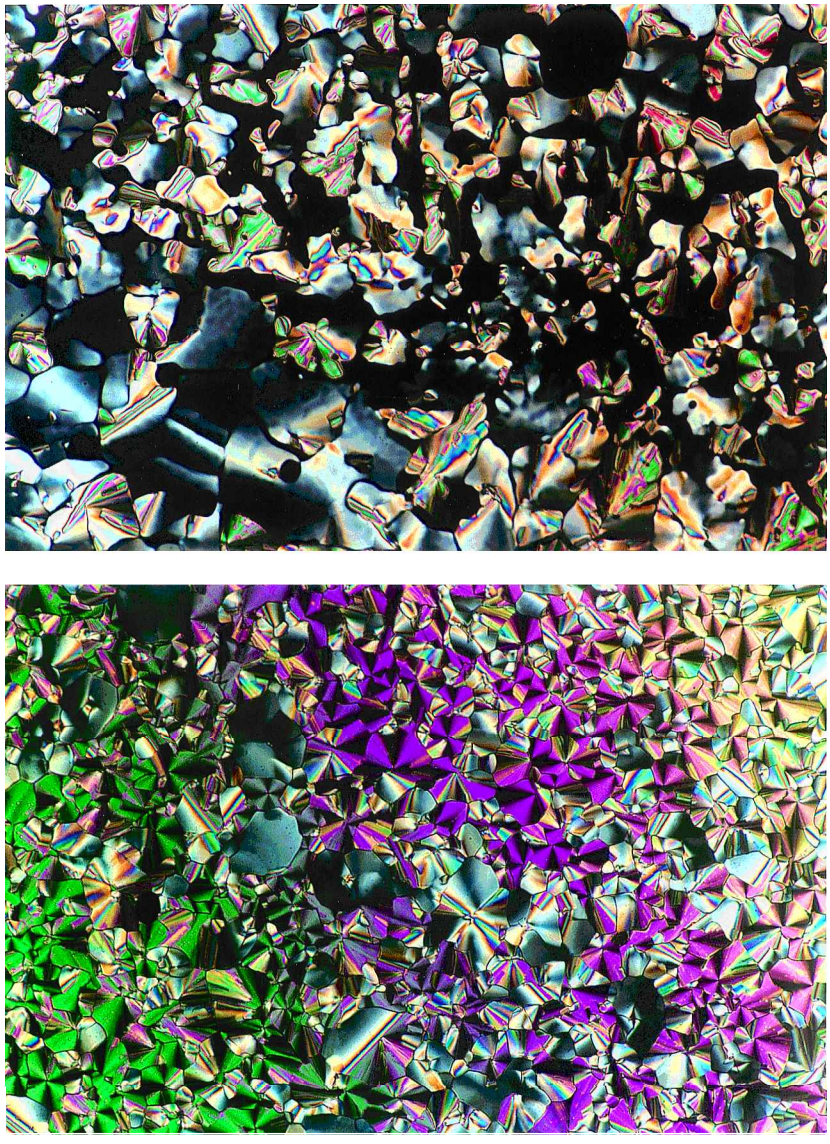


Figure 1. Optical textures (220 X) observed for compound **3a** at 63°C (top) and **3e** at 50°C (bottom).

4.1. *Methyl 4-octadecanoxybenzoate*

White solid; yield 89%. ^{1}H NMR (ppm, $CDCl_3$): 0.82 (t, $-CH_3$, 3H), 1.24–1.84 (m, $-CH_2$, 32H), 3.82 (s, $-OCH_3$, 3H), 3.93 (t, $-OCH_2$, 2H), 6.84 (d, $-C_6H_4$, 2H), 7.97 (d, $-C_6H_4$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.04, 22.57, 25.93, 29.00, 29.14, 31.74, 51.43, 67.95, 113.83, 122.16 (C_1), 131.32, 162.77, 166.53.

4.2. *4-Octadecanoxybenzoic acid*

White solid; yield 95%. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 3H), 1.23–1.83 (m, $-CH_2$, 32H), 3.93 (t, $-OCH_2$, 2H), 6.98 (d, $-C_6H_4$, 2H), 8.02 (d, $-C_6H_4$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 14.03, 22.61, 25.91, 29.04, 2929, 2961, 31.85, 68.71, 114.09, 126.03, 129.69, 162.33, 171.82.

4.3. *Ethyl 3,4-didecanoxybenzoate*

White solid; yield 81%. ^{1}H NMR (ppm, $CDCl_3$): 0.84–0.91 (m, $-CH_3$, 9H), 1.23–1.52 (m, $-CH_2$, 28H), 1.73–1.83 (m, $-CH_2$, 4H), 3.99–4.06 (m, $-OCH_2$, 4H), 4.28–4.38 (q, $-OCH_2$, 2H), 6.83 (d, $-C_6H_3$, 1H), 7.54–7.63 (dd, $-C_6H_3$, 2H). ^{13}C NMR ($CDCl_3$): 13.58, 14.03, 22.31, 25.74, 25.79, 28.99, 29.03, 29.07, 29.11, 29.14, 29.25, 29.27, 29.31, 31.60, 60.26, 69.20, 65.57, 76.05, 76.68, 77.32, 112.74, 115.35, 123.16, 123.38, 148.79, 153.41, 166.16.

4.4. *3,4-Didecanoxybenzoic acid*

White solid; yield 91%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (m, $-CH_3$, 6H), 1.22–1.57 (m, $-CH_2$, 28H), 1.80–1.84 (m, $-CH_2$, 4H), 4.05 (m, $-OCH_2$, 4H), 6.89 (d, $-C_6H_3$,

1H), 7.61–7.74 (m, $-C_6H_3$, 2H), 10.71 (s, br −OH, 1H). ^{13}C NMR ($CDCl_3$): 13.99, 22.65, 26.02, 29.20, 29.32, 29.57, 31.92, 69.28, 69.61, 112.47, 115.38, 121.77, 124.61, 148.90, 154.31, 171.80.

4.5. *Methyl 3,4,5-trioctanoxybenzoate*

Light yellow paste; yield 78%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (t, $-CH_3$, 9H), 1.21–1.42 (m, $-CH_2$, 30H), 1.78 (m, $-CH_2$, 6H), 4.00 (t, $-OCH_2$, 6H), 7.25 (s, $-C_6H_2$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.70, 22.45, 25.88, 29.14, 30.16, 31.63, 51.66, 68.66, 72.86, 107.62, 124.33, 142.13, 152.46, 166.05.

4.6. *3,4,5-Trioctanoxybenzoic acid*

White solid; yield 94%. ^{1}H NMR (ppm, $CDCl_3$): 0.95 (t, $-CH_3$, 9H), 1.22–1.34 (m, $-CH_2$, 30H), 1.85 (m, $-CH_2$, 6H), 4.09 (t, $-OCH_2$, 6H), 7.39 (s, $-C_6H_2$, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.88, 25.51, 25.53, 25.90, 25.94, 29.14, 29.22, 29.36, 30.19, 31.68, 31.75, 68.94, 7332, 108.39, 123.61, 143.00, 152.65, 172.00.

4.7. *3,4,5-Trioctanoxybenzoic acid N-(3,4,5-trioctanoxybenzoyl)hydrazide*

A mixture of 3,4,5-trioctanoxybenzoic acid (1.00 g, 1.97 mmol) and thionyl chloride (10 ml) was heated at reflux for 1 h under nitrogen. Excess thionyl chloride was removed under vacuum, and 3,4,5-trioctanoxybenzoic acid chloride product was used directly for the next step without further purification. Hydrazine hydrate (0.30 g, 5.91 mmol) dissolved in dried dichloromethane (5.0 ml) was added dropwise to a solution of 3,4,5-trioctanoxybenzoic acid chloride dissolved in dichloromethane (6.00 ml) over a period of 2 h. The reaction mixture was stirred at room temperature overnight; it was then concentrated to give a light yellow solid, and the product was obtained as white crystals after recrystallization from hot dichloromethane/methanol. Yield 82%, m.p. 150.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (m, $-CH_3$, 18H), 1.31–1.49 (m, $-CH_2$, 60H), 1.81 (m, $-CH_2$, 12H), 4.01 (m, $-OCH_2$, 12H), 7.33 (s, $-C_6H_2$, 4H), 11.69 (s, −NH, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.89, 22.52, 25.94, 29.15, 29.22, 29.37, 30.19, 31.69, 31.75, 68.94, 73.32, 108.32, 123.71, 142.88, 152.64, 171.90. IR (KBr): 3235, 2921, 2852, 1737, 1689, 1645, 1585, 1467, 1378, 1335, 1218, 1115, 856, 722 cm^{-1}.

4.8. *4-Octadecanoxybenzoic acid N-(4-octadecanoxybenzoyl)hydrazide*

Recrystallization from hot THF gave white crystals; yield 86%, m.p. 129.0°C. ^{1}H NMR (ppm, $CDCl_3$): 0.86 (t, $-CH_3$, 6H), 1.27–1.45 (m, $-CH_2$, 60H), 1.75–1.78 (m, $-CH_2$, 4H), 3.98 (t, $-OCH_2$, 4H), 6.86 (d, $-C_6H_4$, 4H), 7.80 (d, $-C_6H_4$, 4H), 9.45 (s, −NH, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.96, 22.64, 26.04, 29.22, 29.33, 29.38, 29.68, 31.93, 68.44, 114.62, 123.86, 129.22, 162.63, 164.38. IR (KBr): 3208, 2917, 2850, 1595, 1470, 1251, 833, 627 cm^{-1}.

4.9. *3,4-Didecanoxybenzoic acid N-(3,4-didecanoxybenzoyl)hydrazide*

White crystals; yield 94%, m.p. 101.9°C. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (m, $-CH_3$, 12H), 1.31–1.46 (m, $-CH_2$, 56H), 1.80 (m, $-CH_2$, 8H), 4.00 (tt, $-OCH_2$, 8H), 6.83 (d, $-C_6H_3$, 2H), 7.46 (m, $-C_6H_3$, 4H), 9.68 (s, −NH, 2H). ^{13}C NMR (ppm, $CDCl_3$): 13.96, 22.63, 26.05, 29.31, 29.41, 29.44, 29.59, 31.91, 69.35, 69.55, 112.92, 113.16, 120.77, 124.09, 149.32, 152.96, 164.97. IR (KBr): 3152, 2954, 2918, 2850, 1735, 1600, 1563, 1460, 1377, 1266, 1221, 1119, 745 cm^{-1}.

4.10. *2,5-Bis(3,4,5-trioctanoxyphenyl)-1,3,4-oxadiazole*

A mixture of 3,4,5-trioctanoxybenzoic acid *N*-(3,4,5-trioctanoxybenzoyl)hydrazide (0.30 g, 0.30 mmol) and phosphorus oxychloride (0.91 g, 3.00 mmol) was heated gently under reflux in dried toluene for 1 h. Excess phosphorus oxychloride was evaporated off under reduced pressure, and the pasty yellow residue was purified by silica gel chromatography eluting with dichloromethane. A white paste was obtained after recrystallization from cold THF/methanol; yield 68%. ^{1}H NMR (ppm, $CDCl_3$): 0.90 (m, $-CH_3$, 18H), 1.33–1.52 (m, $-CH_2$, 60H), 1.70–1.90 (m, $-CH_2$, 12H), 4.05 (m, $-OCH_2$, 12H), 7.29 (s, $-C_6H_2$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 13.83, 22.47, 25.91, 29.11, 29.19, 29.34, 30.17, 31.64, 31.71, 69.17, 73.26, 105.32, 118.38, 141.16, 153.31, 164.23. IR (KBr): 2924, 2854, 1592, 1557, 1492, 1468, 1339, 1240, 1117, 842, 733 cm^{-1}.

4.11. *2,5-Bis(4-octadecanoxyphenyl)-1,3,4-oxadiazole*

White needle crystals; yield 70%. ^{1}H NMR (ppm, $CDCl_3$): 0.88 (t, $-CH_3$, 6H), 1.27–1.47 (m, $-CH_2$, 60H), 1.74–1.85 (m, $-CH_2$, 4H), 4.03 (t, $-OCH_2$, 4H), 6.99 (d, $-C_6H_4$, 4H), 8.02 (d, $-C_6H_4$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 14.00, 22.66, 26.05, 29.22, 29.34, 29.38, 29.58, 29.69, 31.93, 68.44, 114.67, 115.12, 116.70, 128.59, 161.96, 164.19. IR (KBr): 2915, 2851, 1731, 1611, 1496, 1469, 1377, 1257, 1175, 836, 742 cm^{-1}.

4.12. *2,5-Bis(3,4-didecanoxyphenyl)-1,3,4-oxadiazole*

White powder; yield 58%. ^{1}H NMR (ppm, $CDCl_3$): 0.81 (m, $-CH_3$, 12H), 1.21–1.42 (m, $-CH_2$, 56H), 1.70–1.80 (m, $-CH_2$, 8H), 3.99 (tt, $-OCH_2$, 8H), 6.87 (d, $-C_6H_3$, 2H), 7.51–7.56 (m, $-C_6H_3$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 13.94, 22.60, 26.01, 26.03, 29.27, 29.35, 29.53, 29.57, 31.87, 69.41, 69.77, 112.50, 113.61, 116.81, 120.43, 149.67, 152.44, 164.28. IR (KBr): 2955, 2918, 2850, 1736, 1597, 1499, 1466, 1378, 1277, 1228, 1144, 1107, 859, 722 cm^{-1}.

4.13. *4-Hexyl-3,5-bis(3,4,5-tridecanoxypheny l)-4H-1,2,4-triazole*

Off-white oil; yield 28%. ^{1}H NMR (ppm, $CDCl_3$): 0.75–0.88 (m, $-CH_3$, 21H), 1.03–1.60 (m, $-CH_2$, 90H), 1.70–1.81 (m, $-CH_2$, 14H), 4.01 (m, $-OCH_2$, 12H), 4.01 (m, $-NCH_2$, 2H), 6.82 (s, $-C_6H_2$, 4H). ^{13}C NMR (ppm, $CDCl_3$): 13.73, 14.02, 22.24, 22.62, 25.82, 26.05, 29.29, 29.35, 29.53, 29.58, 29.62, 29.69, 29.98, 30.30, 30.87, 31.86, 44.97, 69.42, 73.51, 107.82, 122.54, 139.87, 153.44, 155.52. IR (neat): 2924, 2854, 1584, 1487, 1467, 1431, 1380, 1332, 1240, 1116, 845, 722 cm^{-1}.

4.14. *4-Phenyl-3,5-bis(3,4,5,-tridecanoxypheny l)-4H-1,2,4-triazole*

Off-white oil; yield 30%. ^{1}H NMR (ppm, $CDCl_3$): 0.89 (m, $-CH_3$, 18H), 1.20–1.60 (m, $-CH_2$, 84H), 1.64–1.71 (m, $-CH_2$, 12H), 3.70 (m, $-OCH_2$, 8H), 3.94 (m, $-OCH_2$, 4H), 6.62 (s, $-C_6H_2$, 4H), 7.19–7.24 (m, $-C_6H_5$, 2H), 7.44–7.47 (m, $-C_6H_5$, 3H). ^{13}C NMR (ppm, $CDCl_3$): 14.07, 22.67, 26.00, 26.05, 29.20, 29.34, 29.37, 29.55, 29.58, 29.63, 29.70, 30.29, 31.43, 31.90, 68.93, 73.40, 107.33, 121.43, 128.24, 129.31, 129.90, 136.18, 139.34, 152.88, 154.45. IR (neat): 2924, 2854, 1586, 1541, 1522, 1467, 1388, 1340, 1245, 1116, 838, 704 cm^{-1}.

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