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Smectic A liquid crystals from dihydrazide derivatives with

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lateral intermolecular hydrogen bonding^{**}

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Abstract—Six dissymmetrical dihydrazide derivatives, N-(4-alkoxybenzoyl)-N'-(4'-nitrobenzoyl) hydrazine (Cn–NO₂) and N-(4-alkoxybenzoyl)-N'-(4'-biphenyl carbonyl) hydrazine (Cn–Ph), were synthesized and investigated by means of differential scanning calorimetry, polarized optical microscopy and wide angle X-ray diffraction. The compounds exhibit smectic A₁ phase. Based on the results of ¹H NMR and variable temperature FT-IR spectroscopy, lateral intermolecular hydrogen bonding between -C=O and -N-H groups was proposed and the effect of hydrogen bonding on the phase transitions was discussed. It was concluded that the combination of lateral intermolecular hydrogen bonding and microphase segregation stabilized the smectic A phase. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen bonding is crucial to mesophase formation and stabilization.^{1–4,7} In the past decade, various types of rod-like,² discotic³ and network⁴ supramolecular liquid crystals based on hydrogen bonding have been reported. However, many efforts have been restricted in the generation of calamitic mesophases with molecules bearing a donor or an acceptor site at their terminals, in which hydrogen bonding along the molecular long axis was utilized to form a new and elongated mesogen to stabilize the mesophase, such as a dimer of aromatic carboxyl acid⁵ or dimerization between the carboxyl acid and pyridyl moieties.⁶ However, lateral intermolecular hydrogen bonding has not been extensively investigated, except a few reports which claimed that it can stabilize the smectic layer structure.⁷

The linear N,N'-bis (4'-decyloxybenzoyl) hydrazide⁸ **1** (Scheme 1) exhibits the unusual phase sequence $Cr \rightarrow Cubic \rightarrow Sm C \rightarrow Isotropic.$ Elongating the terminal alkoxy chains, such as bisubstituted by the cetyloxy chains results in exclusively cubic phase.⁹ The introduction of another

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Scheme 1. The molecular structures of 1-3, Cn-NO₂, and Cn-Ph.

decyloxy chain, for instance in compound **2**, will decrease the linearity of the calamatic molecule, preventing the formation of cubic phase and driving the smectic phase metastable.¹⁰ Continuing to add terminal chains **3** will further enlarge the volume fraction of flexible chains, which gives rise to a more curvature of the aromatic–aliphatic interface, leading to columnar phases.¹⁰ Beginn has investigated the effect of the number of the terminal chains and the structure of the hydrogen bonded rigid core on the mesophases. He concluded that both the molecular shape determined by the substituted chains and the intermolecular hydrogen bonding dramatically affected the type and the stability of the mesophases.¹⁰

Dissymmetric dihydrazide derivatives, with one alkoxy

^{*} CCDC 258072 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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chain as terminal group, exhibit smectic and/or nematic phases. Karamysheva and co-workers have reported the phase transitional properties of the derivatives with different substituents.¹¹ In fact, the introduction of a hydarzide group as linkage or part of the rigid unit to calamitic molecules, for example the dissymmetric dihydrazide derivatives Cn-NO₂ and Cn-Ph synthesized in our laboratory (Scheme 1), can simplify the molecular model, providing an opportunity to investigate the influence of lateral intermolecular hydrogen bonding on the mesophase without the worry of steric effect, as in the system of calamitic molecules with laterally attached hydrophilic groups.7d Herein, we focused on the hydrogen bonding motifs and the thermotropic liquid crystalline properties of Cn-NO₂ and Cn-Ph, to reveal the role of the lateral intermolecular interactions in the formation of the mesophases.

2. Results and discussion

2.1. Crystal structure

The powder X-ray diffraction pattern of C3-NO₂ was recorded at ambient temperature on a Rigaku D/max 2500 PC X-ray diffractometer (reflection, Cu K-alpha1). The 2θ range was 2-35°, measured in steps of 0.02°. The crystal structure determination from the powder diffraction data was carried out using Materials Studio.^T All the diffraction peaks can be indexed as the monoclinic structure, and the unit cell contains two molecules. It belongs to P121 space group and the lattice parameters are a = 17.179(5) Å, b =3.319(2) Å, c = 16.692(8) Å and $\beta = 92.533(8)^{\circ}$. The density calculated was 1.20 g cm⁻³. The final Rietveld refinement gave R_{wp} =7.38% and R_p =5.45% (110 reflections, 1627 data points). Figure 1 illustrated the molecules stacking of $C3-NO_2$ in the crystal. What can be observed directly was that the intermolecular hydrogen bonding was more easily accessible due to the higher linearity of the intermolecular N-H \cdots O bond.¹² The angle of intermolecular hydrogen bond of N-H···O (141.37 and 117.52°) was larger than that of intramolecular one (103.98 and 103.43°).



Figure 1. The crystal structure of C3–NO₂. The dashed line illustrated the hydrogen bonding.

2.2. Hydrogen-bonding motif

In order to explore the hydrogen-bonding motif, temperature dependent FT-IR and ¹H NMR spectroscopic experiments were performed. In ¹H NMR dilution studies, the amide protons of $Cn-NO_2$ and Cn-Ph showed strong concentration dependence, for example, reducing the concentration of C6-NO2 in CDCl3 from 15.6 to 0.2 mM causes both NH-1 (near to nitro phenyl, $\Delta \delta = 0.57$ ppm) and NH-2 (near to alkoxy phenyl, $\Delta \delta = 0.19$ ppm) to shift upfield remarkably, as shown in Table 1. These results strongly indicated that N-H groups were involved in intermolecular hydrogen bonding.¹³ The variable-temperature measurements of amide protons further supported above conclusion. Generally, internally hydrogen bonded amides are expected to show a much smaller shift with temperature ($<3.0\times10^{-3}$ ppm K⁻¹) compared to those directed externally and accessible for hydrogen bonding to a polar solvent (>4.0×10⁻³ ppm K⁻¹).¹⁴ However, both NH-1 and NH-2 of C6–NO₂ showed large shifts (5.85 \times 10^{-3} and 7.74×10^{-3} ppm \tilde{K}^{-1} respectively, as shown in Fig. 2) with temperature in 20% DMSO- d_6 /CDCl₃, suggesting the primary involvement of N-H protons in intermolecular hydrogen bonding. This may be due to a more favorable geometry for the formation of the intermolecular hydrogen bonding than the intramolecular one, as have been discussed in the crystal structure section.

Table 1. The chemical shifts of amide protons for C6–NO₂ at different concentrations in CDCl₃ (NH-1: near to nitro phenyl, NH-2: near to alkoxy phenyl)

Concentration/mM	NH-1 chemical shifts /ppm	NH-2 chemical shifts /ppm
15.6	9.85	9.19
7.8	9.64	9.09
3.9	9.44	9.02
2.6	9.40	9.01
0.2	9.28	9.00
		(continued on next page)



Figure 2. The chemical shifts of NH-1 and NH-2 of C6–NO₂ in 20% DMSO- d_6 /CDCl₃ versus temperature. NH-1: near to nitro phenyl, NH-2: near to alkoxy phenyl.

Position, intensity and shape of IR absorption bands are known to be sensitive to conformations and intermolecular interactions. So, in order to evaluate the effect of hydrogen bonding on the phase transitional properties of the compounds, temperature dependent FT-IR spectra of C16–NO₂ and C16–Ph were measured. Table 2 presented the assignments of infrared frequencies for C16–NO₂ and

[†] The solution of the crystal structure from powder diffraction data was performed on Materials Studio, and the modeling details will be published elsewhere.

Table 2. Assignments of infrared frequencies for C16–Ph and C16– NO_2 at room temperature

Assignments	IR frequencies (cm^{-1})	
	C16–Ph	C16–NO ₂
v (N–H)	3247	3203
ν (Ar-H)	3013	3017
$v_{\rm as}$ (CH ₃), $v_{\rm as}$ (CH ₂)	2954, 2916	2953, 2918
$\nu_{\rm s}$ (CH ₃), $\nu_{\rm s}$ (CH ₂)	2849	2871, 2850
amide I, ν C=O	1684, 1650	1590, 1567
$\nu_{\rm C=C}$ of phenyl ring	1609, 1580	1608, 1578
	1506, 1485	
	1472, 1449	
Amide II, III, $\nu_{\rm C-N} + \delta_{\rm N-H}$	1529, 1297	1493
$\nu_{\rm as}, \nu_{\rm s} (\rm NO_2)$	_	1522, 1345
δ (CH ₂)	1464	1466
ν (Ar-O)	1255	1254
ν (C–O)	1025	1026
δ (Ar-H) _{o.o.p} , para-	845	844
δ (Ar-H) _{0.0,p} , mono-	741, 692	_
$(CH_2)_n$ rocking, $n \ge 4$	720	720

C16-Ph.¹⁵ At room temperature, apart from characteristic bands of aromatic ring at 1609, 1580, 1506, 1485, 1472, 845, 741, and 692 cm^{-1} , C16–Ph exhibits absorptions at 3247 cm⁻¹ (ν (N–H)), 1684, 1650 cm⁻¹ (amide I, $\nu_{C=O}$), and 1529, 1297 cm⁻¹ (amide II, III, $\nu_{C-N} + \delta_{N-H}$). The absorption bands at 2954, 2916 cm⁻¹ (ν_{as} (CH₃, CH₂)), 2872, 2849 cm⁻¹ (ν_{s} (CH₃, CH₂)), 1465 cm⁻¹ (δ (CH₂)), and 720 cm⁻¹ ((CH₂)_n rocking, $n \ge 4$) were attributed to the vibrations of alkoxy chains. The presence of N-H stretching vibrations at 3247 cm^{-1} (the absence of free N-H, a relatively sharp peak with the frequency higher than 3400 cm^{-1}), intense absorption of amide I at 1650 cm^{-1} , and relatively weak absorption at 1684 cm^{-1} clearly indicated that almost all the N-H groups are associated with C=O groups via N-H···O=C hydrogen bonding.¹⁶ For C16-NO₂, the N-H stretching vibration located at 3202 cm^{-1} , amide I at 1590, 1567 cm⁻¹, and characteristic absorption of nitro group at 1522 cm^{-1} (ν_{as} (NO₂)) and 1345 cm⁻¹ (ν_s (NO₂)). The same conclusion can be drawn for C16–NO₂, in spite of the stronger hydrogen bonding confirmed by the red-shift of the N-H and C=O stretching vibrations in C16–NO₂ with respect to C16–Ph. Thus, along with the results of crystal structure, FT-IR, and ¹H NMR dilution experiments, we can get a clear hydrogen-bonding



Figure 3. Schematic hydrogen bonding motifs. The dashed line illustrated the hydrogen bonding.

motif, in which N–H and C=O group were involved in intermolecular hydrogen bonding. The direction of the interaction is perpendicular to the molecular long axis, as depicted in Figure 3a, in contrast to the intramolecular hydrogen bonding pattern speculated by Karamysheva, etc.¹¹ as shown in Figure 3b.

Moreover, these conclusions were further supported by the fact that the v_{N-H} and amide I band became weaker and shifted to higher frequencies upon heating. Figure 4 showed the temperature dependence of $\nu_{\rm N-H}$ of C16–Ph. We found a sharp increase of ν_{N-H} wavenumbers on going from crystalline to smectic A and from smectic A to isotropic liquid. The typical wavenumbers of N-H vibration of C16-Ph are at around 3250, 3295 and 3310 cm^{-1} in the crystalline state, smectic A phase and isotropic phase, respectively. The observed N-H stretching vibration frequency at 3295 cm^{-1} in the smectic A phase and the increase of N–H stretching vibration by ca. 15 cm $^{-1}$ at the isotropic transition strongly indicated that the presence of the hydrogen bonding in the smectic A phase of C16–Ph. Furthermore, this conclusion was also supported by the fact that the blue-shift of C=O stretching vibration was companied by an increase in intensity at around 1655 cm^{-1} , while the absorption at 1690 cm^{-1} diffused and decreased, as shown in Figure 5a. For C16–NO₂, the N-H vibrations shift from 3210 to 3295 cm⁻¹ and the amide I band from 1590, 1567 to 1654, 1688 cm⁻¹, as shown in Figure 5b and c, during the transition from crystalline to smectic A phase. Due to the limitation of infrared spectrometer range, FT-IR spectra of C16-NO₂ in its isotropic phase were not measured. However, based on these observation, we have already been able to draw the same conclusion that the intermolecular hydrogen bonding exists in the smectic A phase, as that of the C16-Ph.



Figure 4. The temperature dependent N–H stretching vibrations of C16– Ph: Cr, Sm A and I indicates crystalline state, smectic A phase and isotropic liquid, respectively.

2.3. Phase behaviors

The phase behaviors of Cn– NO_2 and Cn–Ph were studied by polarized optical microscopy, differential scanning calorimetry and wide angle X-ray diffraction. Their transitional temperatures and associated enthalpies were summarized in Table 3. The molecules of Cn– NO_2 and Cn–Ph exhibited enantiotropic smectic A behavior with a fan-shaped texture



Figure 5. The temperature dependent FT-IR spectra at the interval of 15 °C. (a) C16–Ph at the range of $1450-1750 \text{ cm}^{-1}$, (b) C16–NO₂ at the range of $3000-3600 \text{ cm}^{-1}$, (c) C16–NO₂ at the range of $1450-1750 \text{ cm}^{-1}$.

(as shown in Figure 6). In the thermodynamic studies, it should be noticed that remarkably stable smectic A phase was obtained, which was characterized by wide mesophase ranges (even broader than 110 °C), high clearing points (as

Table 3. Transition temperatures and enthalpies of Cn-NO2 and Cn-Ph



Figure 6. The fan-shaped texture (\times 400) of C3–NO₂ at 193 °C in the cooling run.

high as 268 °C) and large isotropic transition enthalpy (>6 kJ/mol). The high stability of the smectic A phase may be ascribed to the combination of lateral intermolecular hydrogen bonding and microphase segregation. Firstly, the large transitional enthalpies implied that strong attractive force still existed in the smectic A phase. This might be due to the lateral hydrogen bonding, as have been confirmed by the temperature dependent FT-IR spectroscopic study. The presence of intermolecular cohesive forces within the layer may have stabilized the parallel alignment of the smetogen in the layer structures.⁷ Secondly, the clearing points rise, the transition enthalpies increase, and the mesophase ranges broaden with the elongating terminal chain. This may be explained as the elongation of the terminal chains increased the microphase segregation effect by enhancing the incompatibility between the hydrogen bonded rigid aromatic rings and flexible alkoxy chains. Such microsegregation effect was considered to be the driving force for the formation of smectic phase.¹⁷ Moreover, the hydrogen bonding and the strong dipole substitute were considered to enhance the incompatibility. Therefore Cn-NO₂ has higher thermal stability than Cn-Ph. Additionally, the clearing point increased while the melting temperature decreased with the elongation of alkoxy chain (see Table 3), which suggested that the terminal chains have bigger impact on the melting process than that on the isotropic transition. The elongating alkoxyl chain may be favorable to the formation of the mesophase by decreasing the melting point, whereas the stability of the mesophase must be ascribed to the

Compound	Transition ^a	$T/^{\circ}$ C heating ($\Delta H/kJ \text{ mol}^{-1}$)	$T/^{\circ}$ C cooling ($\Delta H/kJ \text{ mol}^{-1}$)
C3–NO ₂	Cr–Sm A	208.2(19.86)	184.0(21.12)
	Sm A–I	232.8(6.54)	230.3(6.32)
C6–NO ₂	Cr–Sm A	172.2(19.17)	158.2(18.84)
	Sm A–I	259.5(9.07)	257.82(8.16)
C12-NO ₂	Cr–Sm A	144.2(14.90)	139.3(11.04)
	Sm A–I	262.5(13.90)	263.1(8.21)
C16-NO ₂	Cr–Sm A	146.3(8.86)	141.2(11.30)
	Sm A–I	260.6(12.14)	258.8(8.87)
C12–Ph	Cr–Sm A	147.7(36.53)	117.2(9.90) ^b
	Sm A–I	208.6(4.76)	204.0(4.39)
C16–Ph	Cr–Sm A	145.2(57.37)	113.3(66.09)
	Sm A–I	210.9(7.48)	208.6(7.22)

^a Cr, Sm A and I indicate crystalline state, Smectic A phase and isotropic liquid, respectively.

^b The small enthalpy was due to another phase transition observed below the melting process.

presence of attractive force or the combination of the two. Thus, based on these analyses, we can conclude that combination of the lateral intermolecular hydrogen bonding and microphase segregation played an important role in generating the stable smectic phase.

2.4. Mesophase structure

X-ray diffraction measurements have been performed on the mesophases of Cn–NO₂ and Cn–Ph. Characteristic patterns of smectic A phase with sharp peaks at lower angle region and a broad halo at higher angle region (about 20°) were observed, as shown in Fig. 7. The layer spacing values (*d*) collected in the Table 4, were almost independent to the temperature. The *d*-spacings of Cn–NO₂ in their mesophases were 2–5 Å longer than the calculated molecular



Figure 7. X-ray diffraction patterns of dissymmetric dihydrazide derivatives: (a) C6–NO₂ at 190 °C, (b) C16–Ph at 170 °C.

Table 4. Summary of X-ray diffraction results of Cn-NO2 and Cn-Ph

Compound	Molecular length ^a (<i>l</i>)/Å	T/°C	Layer spacing (d)/Å	d/l
C3–NO ₂	19.5	225	21.4, 10.9	1.10
C6-NO ₂	22.5	190	25.4	1.13
C12-NO ₂	30.0	160	33.5	1.12
C16-NO ₂	34.6	200	39.4, 19.7	1.14
C12-Ph	32.6	190	32.7	1.00
C16–Ph	37.4	170	36.2, 18.1	0.97

^a Molecular length was calculated by MM2.

lengths (*l*). These *dll* ratios were from 1.10 to 1.14, while the layer spacings of Cn-Ph were almost equal to the molecular lengths. These results indicated that the molecules of Cn-NO₂ and Cn-Ph kept a Semectic A₁ arrangement in their liquid crystalline phases.¹⁸

3. Conclusion

Lateral intermolecular hydrogen bonding was considered undesirable for the calamitic mesogenic materials, because it could lead to a high melting temperature. However, high stable smectic A phase was generated from these dissymmetric dihydrazide derivatives. Based on our investigations, the presence of intermolecular attractive force in the semectic A phase may enhance the parallel alignment and the combination of lateral intermolecular interaction and microphase segregation effect may be the leading contribution to the stable smectic phase. In fact, lateral hydrogen bonding has been applied to main chain liquid crystal polymers to obtain high mechanical strength, and to LB films to stabilize the layer structure. In conclusion we hope that more attention will be paid to exploit the potential use of the lateral hydrogen bonding in materials science. Now the investigations using Cn-Ph and Cn-NO2 as organogelators are in progress.

4. Experimental

4.1. Synthesis

Cn-NO₂ and Cn-Ph were synthesized according to the route shown in Scheme 2. 4-Nitrobenzoyl chloride or 4-biphenyl carbonyl chloride was reacted with 4-alkoxyl-benzoylhydrazine in THF at room temperature for 8 h, yielding the products of Cn-NO₂ and Cn-Ph. All the compounds were purified by a recrystallization from methanol or alcohol for further NMR, FT-IR, measurements and elemental analysis.



Cn NO₂: R⁵ = NO₂, n = 3,6,12,16 Cn Ph: R⁵ = phenyl, n = 12,16

Scheme 2. The synthesis of Cn–NO₂ and Cn–Ph.

4.1.1. *N*-(**4**-**Propyloxybenzoyl**)-*N'*-(**4**'-**nitrobenzoyl**) **hydrazine** (**C3–NO**₂). ¹H NMR (500 MHz, DMSO), (ppm, from TMS): 10.83 (s, 1H); 10.50 (s, 1H); 8.39 (d, 2H, *J*=7.9 Hz); 8.15 (d, 2H, *J*=7.7 Hz); 7.90 (d, 2H, *J*= 8.1 Hz); 7.06 (d, 2H, *J*=7.9 Hz); 4.02 (t, 2H, *J*=5.7 Hz); 1.78–1.74 (m, 2H); 0.99 (t, 3H, *J*=6.9 Hz). FT-IR (KBr disc, cm⁻¹): 3205, 2964, 2937, 2879, 2855, 1609, 1593, 1566, 1527, 1495, 1465, 1416, 1393, 1345, 1317, 1255, 1175, 1111, 1066, 1011, 977, 866, 842, 819, 758, 724, 714, 702, 684, 657, 639, 622. Anal. calcd for $C_{17}H_{17}N_3O_5$: C, 59.47; H, 4.99; N, 12.24. Found C, 59.57; H, 4.78; N, 12.18.

4.1.2. *N*-(**4**-Hexyloxybenzoyl)-*N'*-(**4**'-nitrobenzoyl) hydrazine (C6–NO₂). ¹H NMR: (500 MHz, DMSO), (ppm, from TMS): 10.79 (s, 1H); 10.47 (s, 1H); 8.38 (d, 2H, J=8.6 Hz); 8.14 (d, 2H, J=8.4 Hz); 7.90 (d, 2H, J= 8.5 Hz); 7.05 (d, 2H, J=8.6 Hz); 4.05 (t, 2H, J=6.2 Hz); 1.75–1.71 (m, 2H); 1.43–1.40 (m, 2H), 1.34–1.32 (m, 4H), 0.86 (t, 3H, J=6.4 Hz). FT-IR (KBr disc, cm⁻¹): 3196, 2932, 2857, 1609, 1592, 1568, 1525, 1495, 1467, 1396, 1344, 1317, 1253, 1175, 1110, 1030, 866, 846, 759, 723, 702, 661, 623. Anal. calcd for C₂₀H₂₃N₃O₅: C, 62.33; H, 6.02; N, 10.90. Found C, 62.56; H, 5.71; N, 10.68.

4.1.3. *N*-(**4**-Dodecyloxybenzoyl)-*N'*-(**4**'-nitrobenzoyl) hydrazine (C12–NO₂). ¹H NMR (500 MHz, DMSO), (ppm, from TMS): 10.79 (s, 1H); 10.47 (s, 1H); 8.38 (d, 2H, *J*=8.4 Hz); 8.15 (d, 2H, *J*=8.5 Hz); 7.90 (d, 2H, *J*= 8.5 Hz); 7.04 (d, 2H, *J*=8.4 Hz); 4.04 (t, 2H, *J*=6.2 Hz); 1.74–1.70 (m, 2H); 1.42–1.40 (m, 2H); 1.33–1.25 (m, 16H); 0.86 (t, 3H, *J*=6.4 Hz). FT-IR (KBr disc, cm⁻¹): 3202, 2920, 2851, 1609, 1591, 1567, 1523, 1494, 1466, 1395, 1345, 1318, 1254, 1172, 1109, 1028, 1010, 871, 844, 810, 759, 721, 699, 682, 658, 638, 623. Anal. calcd for C₂₆H₃₅N₃O₅: C, 66.50; H, 7.51; N, 8.95. Found C, 66.70; H, 7.71; N, 9.07.

4.1.4. *N*-(**4**-Cetyloxybenzoyl)-*N'*-(**4**'-nitrobenzoyl) hydrazine (C16–NO₂). ¹H NMR (500 MHz, DMSO), (ppm, from TMS): 10.81 (s, 1H); 10.49 (s, 1H); 8.38 (d, 2H, *J*=8.6 Hz); 8.15 (d, 2H, *J*=8.6 Hz); 7.90 (d, 2H, *J*= 8.6 Hz); 7.04 (d, 2H, *J*=8.7 Hz); 4.04 (t, 2H, *J*=6.4 Hz); 1.74–1.71 (m, 2H); 1.41–1.40 (m, 2H); 1.32–1.24 (m, 24H); 0.85 (t, 3H, *J*=6.7 Hz). FT-IR (KBr disc, cm⁻¹): 3203, 2919, 2850, 1608, 1591, 1567, 1523, 1493, 1466, 1394, 1346, 1318, 1254, 1172, 1109, 1027, 872, 844, 810, 758, 720, 698, 658, 637, 622. Anal. calcd for C₃₀H₄₃N₃O₅: C, 68.54; H, 8.24; N, 7.99. Found C, 68.76; H, 8.41; N, 8.05.

4.1.5. *N*-(**4**-Dodecyloxybenzoyl)-*N*'-(**4**'-biphenyl carbonyl) hydrazine (C12–Ph). ¹H NMR: (500 MHz, DMSO) (ppm, from TMS): 10.53 (s, 1H); 10.40 (s, 1H); 8.02 (d, 2H, J= 8.1 Hz); 7.91 (d, 2H, J=8.6 Hz); 7.84 (d, 2H, J=8.1 Hz); 7.77 (d, 2H, J=7.5 Hz); 7.52 (t, 2H, J=7.5 Hz); 7.43 (t, 1H, J=7.3 Hz); 7.05 (d, 2H, J=8.6 Hz); 4.04 (t, 2H, J= 6.3 Hz); 1.75–1.72 (m, 2H); 1.42–1.41 (m, 2H); 1.32–1.25 (m, 16H); 0.86 (t, 3H, J=6.5 Hz). FT-IR (KBr disc, cm⁻¹): 3233, 3053, 2954, 2936, 2858, 1678, 1643, 1609, 1579, 1535, 1507, 1485, 1448, 1393, 1296, 1253, 1181, 1111, 1076, 1038, 1013, 898, 846, 742, 696. Anal. calcd for C₃₂H₄₀N₂O₃: C, 76.77; H, 8.05; N, 5.60. Found C, 76.73; H, 8.30; N, 5.65. **4.1.6.** *N*-(**4**-Cetyloxybenzoyl)-*N'*-(**4**'-biphenyl carbonyl) hydrazine (C16–Ph). ¹H NMR: (500 MHz, DMSO) (ppm, from TMS): 10.46 (s, 1H); 10.33 (s, 1H); 8.01 (d, 2H, J= 8.4 Hz); 7.89 (d, 2H, J=8.8 Hz); 7.82 (d, 2H, J=8.4 Hz); 7.75 (d, 2H, J=7.4 Hz); 7.50 (t, 2H, J=7.6 Hz); 7.41 (t, 1H, J=7.3 Hz); 7.02 (d, 2H, J=8.8 Hz); 4.03 (t, 2H, J= 6.5 Hz); 1.73–1.70 (m, 2H); 1.42–1.39 (m, 2H); 1.31–1.23 (m, 24H); 0.84 (t, 3H, J=6.9 Hz). FT-IR (KBr disc, cm⁻¹): 3247, 3013, 2964, 2916, 2849, 1684, 1650, 1609, 1580, 1529, 1506, 1485, 1472, 1464, 1449, 1396, 1297, 1255, 1181, 1109, 1025, 1006, 924, 895, 845, 741, 720, 685. Anal. calcd for C₃₆H₄₈N₂O₃: C, 77.66; H, 8.69; N, 5.03. Found C, 77.63; H, 8.81; N, 5.02.

4.2. Characterization

¹H NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer, using chloroform-*d* or DMSO-*d*6 as solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded with a Perkin–Elmer spectrometer (Spectrum One B). The sample was pressed tablet with KBr. Phase transitional properties were investigated by a Mettler Star DSC 821^e. Texture observation was conducted on a Leica DMLP polarized optical microscope equipped with a Leitz 350 microscope heating stage. X-ray diffraction was carried out with a Rigaku D/max 2500 PC X-ray diffractometer.

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