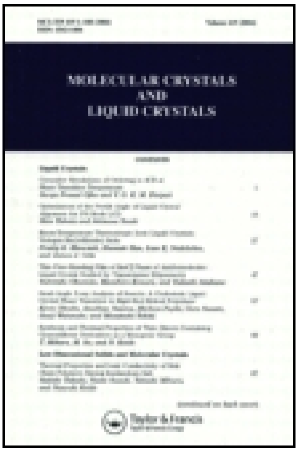

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TEMPO Containing Esters and Their Magnetic and Liquid Crystal Properties

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TEMPO Containing Esters and Their Magnetic and Liquid Crystal Properties

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*Six new magnetic liquid crystals have been prepared, in which trans-bicyclohexyl or trans-cyclohexyl phenyl and biphenyl carboxylic acid phenyl bis-ester mesogenic cores with n-propyl and n-pentyl substituents were terminated by 4-amino-TEMPO (TEMPO=2, 2, 6, 6-tetramethyl piperidine-1-oxyl). All the compounds have been characterized on the basis of their spectral datum. Determined by superconducting quantum interference device (SQUID), electron paramagnetic resonance (EPR), differential scanning calorimeter (DSC), and hot stage polarizing optical microscope (HS-POM), the compounds have both magnetic and liquid crystalline properties. Their temperature ranges of mesophase are about 3.0°C–6.0°C and the susceptibility is 0.137 emu K mol^{-1} and θ is –5.54 K for **7a** between 135 K and 185 K.*

Keywords 4-Amino-TEMPO; ester; liquid crystals; magnetic; phase transition temperature

1. Introduction

Investigation of the relationship between molecular structure and properties is an essential task of materials chemistry. Modification of molecular structures to allow them to fast response to outer stimuli such as magnetism, thermal, and light is an important path way to innovate new materials. Liquid crystals have been successfully used in the information field duo to its quick response to the electric signal and thereby to change optical action [1,2]. However, the magnetic properties of liquid crystal seem no significance because of the small diamagnetic susceptibility anisotropy ($0<\square\Delta\chi\mathrm{dia}\square<60 \times 10\text{-}6$ emu mol^{-1}) of

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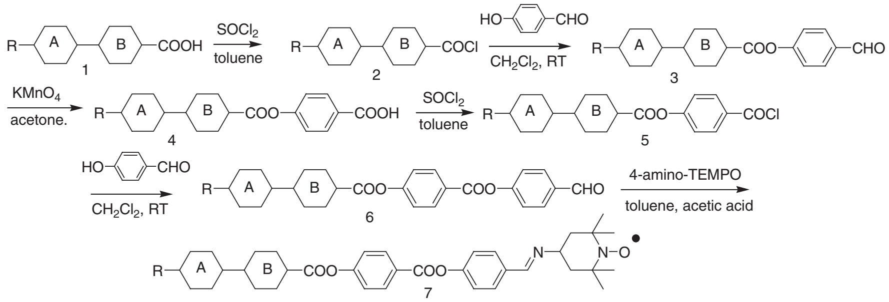
*Address correspondence to Zhong-Wei An, Key Laboratory of Applied Surface and Colloid Chemistry, MOE, School of Chemistry & Materials Science, Shaanxi Normal University, Xi'an, Shaanxi 710062, China. Tel.: +86-29-85308090; Fax: +86-29-85308090. E-mail: gmecazw@126.com the mesogen which arises from the constituent aromatic rings [3]. The development of spin system with liquid crystalline properties is particularly interesting because of the spin interaction in the oriented molecular aggregates and/or the alteration of magnetic property through the phase transition [4]. It is known that stable organic radicals are generally unsuitable for synthesis of liquid crystals mainly due to inappropriate substitution patterns or the geometry and bulkiness of radical stabilizing substituents, which are detrimental to mesophase stability [5,6]. Much efforts have been paid on this attempt [7], but only a few organic radicals with less bulky DOXYL(4,4-dimethyl-3-oxazolidinyloxy) substituent [8,9] and 3,4-dihydro-2,5-dimethyl-2H-pyrrole-1-oxide [4] have been reported to show liquid crystal behavior. Their molecular structures were limited to those containing a nitroxyl group embedded into the molecular skeleton. To favor the overturn of the rod-like molecules under magnetic field, it has been thought that the stable radical should be located at one terminal of the molecule and a flexible chain connected to the other end. Unfortunately, all attempts to prepare such a mesogen by using the organic spin as terminal group have been unsuccessful except for only one molecule existing as a monotropic mesophase (on cooling process) [6]. According to our previous experience [10–12], the long rigid core is able to result into a stable mesophase and even to covert the nematic phase into the smectic one by increasing the number of its units. A common strategy to limit the smectic phase is an introduction of a lateral group [13] into the molecule. All of these provide a possibility to prepare molecules with long rigid core and termination by bulky nitroxyl group and thereby to form liquid crystalline phase, especially a nematic phase, which is extremely interested because it may be useful as a dopant in the practically used liquid crystal mixtures to improve their order parameter and elastic properties [14,15]. Based on our previous studies [11], six new compounds with magnetic group (TEMPO) were designed and synthesized. Our preparative procedure is shown as Scheme 1.



a: R=n-propyl, A=trans-cyclohexyl, B=Phenyl. b: R=n-propyl, A=trans-cyclohexyl, B=trans-cyclohexyl. c: R=n-propyl, A=phenyl, B=phenyl. d: R=n-pentyl, A=trans-cyclohexyl, B=phenyl. e: R=n-pentyl, A=trans-cyclohexyl, B=trans-cyclohexyl f: R=n-pentyl, A= phenyl, B=phenyl.

Scheme 1. The synthesis process of resulting compounds.

2. Experimental

2.1. Instruments and Conditions

The purities of compounds were detected by LC-10A (Shimadzu) instrument with methanol as eluent and flowing rate was 1 mL/min. Elemental analysis was conducted by PE-2400 analyzer (Perkin Elmer). UV spectra were determined by SPECORD 50 spectrometer (Analytik Jena). IR (KBr) spectra were recorded on a Prestige-21 FTIR spectrophotometer (Shimadzu). Mass data were recorded on a GCMS-QP2010 (Shimadzu) and IE was 70 eV. ^{1}H NMR data were obtained on a BRUCKER Avance 500 spectrometer (500 MHz, solvent $CDCl_3$). The DSC experiments were carried out on MDSC Q1000 instrument (TA) and the determination conditions were: the sample mass less than 5 mg; heating rate, 10°C /min in distance far from the transition and 2°C /min before 10°C at the transition, and samples were protected by nitrogen. All images of textures were taken on a LV100POL Polarizing Optical Microscopy (Nikon) with LTS 350 thermoplate (Linkan) and heating rate 1°C /min. EPR spectra were obtained on ER200DSRC10/12 (Bruker) and the determined condition was: frequency 100 KHz, field modulation intensity 2G, and time constant 0.5 s. The temperature susceptibility was obtained by MPMS XL-7 SQUID (Superconducting Quantum Interference Device; Quantum Design) at a field 2000 Oe.

2.2. Synthesis

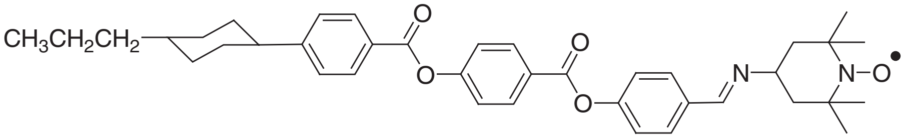
All initial intermediates used in the synthesis were prepared in our laboratory with purity higher than 99%, and characterized by IR, GC-MS, and ^{1}H NMR methods. 4-Amino-TEMPO and other reagent from commercial sources were used without further purification.

*2.2.1. Synthesis of Compounds **2** and **3**.* Compound **2a** was prepared by stirring a mixture of **1a** (1.23 g, 5 mmol), $SOCl_2$ (0.59 g, 5 mmol), and several drops of DMF in toluene (30 mL) at ambient temperature for 5 h, then the solvent was removed under reduced pressure. A brown liquid (**2a**) was obtained and used to next step without further purifying. Compound **3a** was obtained by dissolving **2a** in CH_2Cl_2 (20 mL) and dropped the mixture into a solution of p-hydroxylbenzen aldehyde (0.61 g, 5 mmol) and triethylamine (0.9 mL, 5 mmol) in CH_2Cl_2 (40 mL) and stirred at ambient temperature for 12 h, then the reacting mixture was washed with 5% (mass fraction) NaOH and water. After being dried by Na_2SO_4, the solvent was removed under reduced pressure. The residue was recrystallized with ethanol and a white crystal (**3a**, 1.57 g) was then obtained in yield of 90% (two steps). The Compounds **3b**, **3c**, **3d**, **3e**, and **3f** were also prepared by the same procedure, and their yields were 90%, 88%, 87%, 84%, 85%, and 88%, respectively.

*2.2.2. Synthesis of Compound **4**.* Compound **4a** was obtained by using **3a** (1.57 g, 4.5 mmol) with $KMnO_4$ (1.41 g, 9 mmol) as an oxidant in acetone solution and heating to reflux for 4 h. After being acidified, filtered and washed with water, the residue was recrystallized by acetone, **4a** (1.37 g) was obtained as a white crystal yield of 83%. The other acids **4b**, **4c**, **4d**, **4e**, and **4f** were prepared by the same procedure above and their yields were 87%, 85%, 81%, 83%, and 83%, respectively.

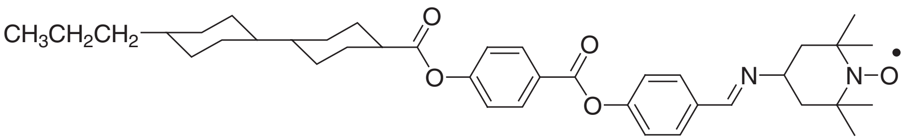
*2.2.3. Synthesis of Compounds **5** and **6**.* Compound 5a was obtained as a pale green solid by using **4a** (1.37 g, 3.7 mmol), repeated the same chlorinating process as **2a** and **6a** was obtained from **5a** by repeated esterifying process as **3a**. The reacting solution was washed with 5% (mass fraction) NaOH and water and dried by Na_2SO_4. After the solvent was removed under reduced pressure, the residue was recrystallized by ethyl acetate, and a white crystal (**6a**) was gained in yield of 82%. Compounds **6b**, **6c**, **6d**, **6e**, and **6f** were prepared in the same process as **6a** with a yield of 80%, 79%, 78%, 75%, 77%, and 75%, respectively.

2.2.4. Synthesis of Compound 7. Compound **7a** was prepared by heating and stirring a mixture of **6a** (0.51 g, 1.1 mmol), 4-amino-TEMPO (0.2 g, 1.1 mmol), and several drops of acetic acid in 30 mL of toluene under reflux temperature for 2 h. After the solvent was removed under reduced pressure, an orange solid was obtained. The crude product was purified by a silica gel column chromatography by using THF as an eluent, and then recrystallized from acetone. A yellow powder (**7a**) 0.44 g was obtained in yield of 64%. By following the same process, other resulting compounds **7b**, **7c**, **7d**, **7e**, and **7f** were also obtained as yellow powder in yield of 65%, 66%, 63% 62%, and 65%, respectively. The characterization data of those homologous series from **7a** to **7f** are summarized as follows.



Structural formula (1)

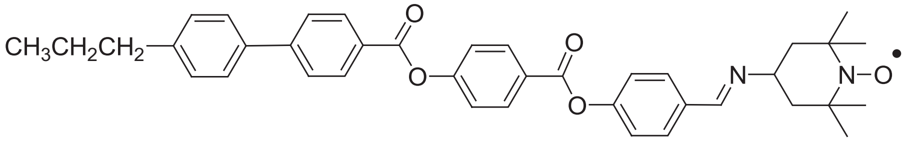
2, 2, 6, 6-tetramethyl-4-(4-(4-(4-(4-*n*-propylcyclohexyl) benzoyloxy) benzoyloxy) benzalamido) piperidine oxygen free radicals (1), Relative molecular mass: 623.75, the mass fraction detected by LC is 98.7%, yield: 64.1%, yellow powder, M.p. 170°C—171°C; Anal. Calcd for $C_{39}H_{47}N_2O_5$: C 75.09, H 7.59, N 4.50; found: C 74.93, H 7.71, N 4.49; IR(KBr)ν: 3107, 3072(m, C—H), 2926, 2848(s, C—H), 1739(vs, C=O), 1643(m, C=N), 1602, 1510, 1458(m, ArH), 1389(w, N—O), 1354(w, C—N), 1307, 1165, 1058(vs, C—O—C), 1265, 1193(s, (CH3)2C=), 974(s, *trans*-H—C=N—R), 852, 802(w, 1, 4-Ar), 692(w, (CH2)n)cm^{-1}; MS (70 ev) *m/z* (%): 623(M+, 1.02), 595(6.81), 593 (18.96), 538(2.49), 495(1.40), 473(6.06), 418(4.99), 365(1.84), 349(7.24), 310(1.15), 275(1.08), 260(2.71), 245(3.25), 230(17.02), 229(100), 201(1.57), 190(5.96), 174(6.65), 148(4.35), 140(13.91), 133(9.42), 124(84.23), 121(18.82), 91(11.86), 77(6.81), 67(5.96), 58(18.61), 51(11.75), 44(26.53), 41 (10.83).



Structural formula (2)

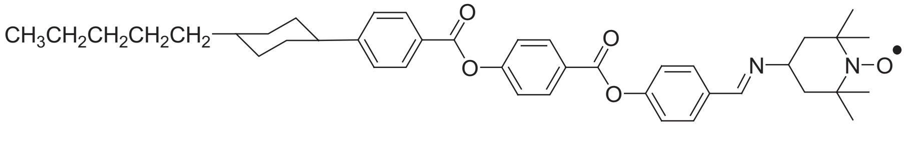
2, 2, 6, 6-tetramethyl-4-(4-(4-(4-(4-*n*-propylcyclohexyl) cyclohexylacyloxy) benzoyloxy) benzylidene amino) piperidine oxygen free radicals (2), Relative molecular mass: 629.72, the mass fraction detected by LC is 98.0%, yield: 65.7%, yellow powder, M.p.

161°C—163°C; Anal. Calcd for $C_{39}H_{53}N_2O_5$: C 74.36, H 8.48, N 4.45; found C 74.29, H 8.81, N 4.43; IR(KBr)ν: 3111(m, C—H), 2926, 2858(s, C—H), 1757, 1730(vs, C=O), 1643(m, C=N), 1597, 1502, 1452(m, ArH), 1385(w, N—O), 1375(w, C—N), 1265, 1161, 1122, 1072(vs, C—O—C), 1199(s, $(CH_3)_2C=C$), 985(s, *trans*-H—C=N—R), 831, 802(w, 1, 4-Ar), 682(w, $(CH_2)n$)cm^{-1}; MS (70 ev) *m*/*z* (%): 631(M+2, 0.94), 630(M+1, 3.02), 629(M+, 3.64), 599(30.99), 597(2.83), 573(0.21), 556(1.06), 544(10.89), 542(1.42), 516(0.53), 490(0.70), 476(0.32), 430(0.06), 395(0.43), 380(0.15), 356(1.84), 355(7.26), 327(0.31), 310(1.59), 294(0.28), 276(0.31), 252(1.16), 235(1.08), 207(1.52), 188(1.80), 156(3.00), 140(15.89), 138(2.77), 124(69.07), 121(100), 98(8.43), 83(8.43), 69(17.05), 67(7.19), 58(16.73), 55(15.84), 41(8.08), 44(1.31).



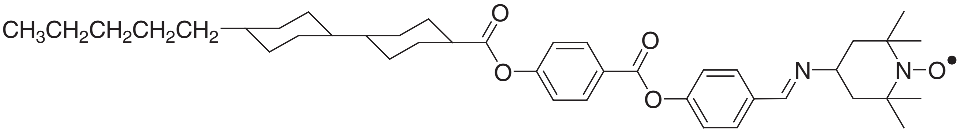
Structural formula (3)

2, 2, 6, 6-tetramethyl-4-(4-(4-(4-(4-*n*-propylphenyl) benzoyloxy) benzoyloxy) benzylidene amino) piperidine oxygen free radicals (3), Relative molecular mass: 617.31, the mass fraction detected by LC is 98.2%, yield: 63.2%, yellow powder, M.p. 157°C—159°C; Anal. Calcd for $C_{39}H_{41}N_2O_5$: C 75.83, H 6.69, N 4.53; found C 75.58, H 6.85, N 4.47; IR(KBr)ν: 3106, 3072(m, C—H), 2959, 2930, 2870(s, C—H), 1742(vs, C=O), 1653(m, C=N), 1601, 1558, 1506, 1456(m, ArH), 1384(m, N—O), 1361(m, C—N), 1273, 1159, 1069(vs, C—O—C), 1199(s, $(CH_3)_2C=C$), 979(s, *trans*-H-C=N-R), 841(w, 1, 4-Ar)cm^{-1}; MS (70 ev) *m*/*z* (%): 619(M+2, 0.10), 618(M+1), 617(M+, 0.53), 602(0.35), 585(3.12), 587(36.35), 585(3.12), 545(0.09), 530(0.45), 504(1.49), 483(0.72), 467(1.14), 395(0.10), 381(0.14), 365(2.73), 343(8.24), 315(0.90), 282(0.11), 240(2.88), 223(77.63), 211(6.95), 194(1.13), 165(8.09), 140(12.01), 124(100), 121(7.44), 98(98.1), 82(2.91), 58(18.56), 42 (5.3).



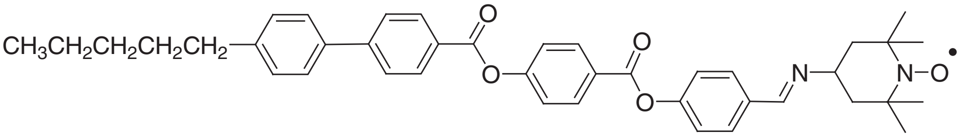
Structural formula (4)

2, 2, 6, 6-tetramethyl-4-(4-(4-(4-(4-*n*-pentylcyclohexyll) benzoyloxy) benzoyloxy) benzylidene amino) piperidine oxygen free radicals (4), Relative molecular mass: 651.38, the mass fraction detected by LC is 98.9%, yield: 62.4%, yellow powder, M.p. 172°C—174°C; Anal. Calcd for $C_{41}H_{51}N_2O_5$: C 75.54, H 7.89, N 4.30; found C 75.40, H 7.74, N 4.23; IR(KBr)ν: 3103(m, C—H), 2954, 2921, 2849(s, C—H stretching vibration), 1740, 1737(vs, C=O), 1641(m, C=N), 1602, 1506, 1458(m, ArH), 1384(w, N-O), 1361(w, C—N), 1263, 1165, 1059(vs, C—O—C), 1215, 1197(s, $(CH_3)_2C=C$), 972(s, *trans*-H—C=N—R), 841(w, 1,4-Ar), 704(w, $(CH_2)n$)cm^{-1}; MS (70 ev) *m*/*z* (%): 621(0.07), 587(0.04), 538(0.48), 523(0.04), 377(37.10), 375(0.20), 343(0.10), 319(0.01), 319(0.01), 305(0.03), 274(0.07), 257(100), 255(2.09), 223(0.91), 199(0.29), 185(0.69), 161(0.50), 145(1.00), 131(2.98), 124(0.72), 121(3.27), 105(0.31), 91(5.04), 77(1.29), 55(2.42), 432(1.75), 29(0.61).



Structural formula (5)

2, 2, 6, 6-tetramethyl-4-(4-(4-(4-(4-*n*-pentylcyclohexyl) cyclohexylacyloxy) benzoyloxy) benzylidene amino) piperidine oxygen free radicals (5), Relative molecular mass: 657.44, mass fraction detected by LC is 98.1%, yield: 66.2%, yellow powder, M.p. 176°C—178°C; Anal. Calcd for $C_{44}H_{57}N_2O_5$: C 74.85, H 8.73, N 4.26; found C 74.90, H 8.86, N 4.20; IR(KBr)ν: 3076(m, C—H), 2926, 2850(s, C—H), 1743(vs, C=O), 1643(m, C=N, 1598, 1452(m, ArH), 1373(w, N—O), 1351(w, C—N), 1263, 1161, 1124, 1074(vs, C—O—C), 1195(s, $(CH_3)_2C{=}C$), 985(s, *trans*-H—C=N—R—), 866(w, 1, 4-Ar)cm^{-1}; MS (70 ev) *m*/*z* (%): 659(M+2, 0.41), 658(M+1, 1.26), 657(M+, 47.68), 599(0.40), 572(3.04), 544(1.89), 529(0.34), 504(0.18), 473(0.12), 430(0.08), 395(0.31), 383(4.18), 381(0.30), 365(3.39), 310(0.81), 294(0.14), 280(1.07), 262(1.20), 245(1.51), 188(0.79), 140(22.09), 138(4.17), 124(100), 121(61.34), 109(4.89), 98(1.58), 91(1.23), 83(15.57), 79(2.70), 69(8.28), 58(23.09), 55(15.36), 44(1.87), 41(6.61).



Structural formula (6)

2, 2, 6, 6-tetramethyl-4-(4-(4-(4-*n*-pentylphenyl) benzoyloxy) benzoyloxy) benzylidene amino) piperidine oxygen free radicals (6), Relative molecular mass: 645.81; the mass fraction detected by LC is 98.3%, yield: 63.7%, yellow powder, M.p. 171°C—172°C; Anal. Calcd for $C_{44}H_{45}N_2O_5$: C 76.25, H 7.02, N 4.34; found C 76.48, H 7.16, N 4.48; IR(KBr)ν: 3078(m, C—H), 2964, 2927, 2858(s, C—H), 1737(vs, C=O), 1643(m, C=N), 1642, 1602, 1502(m, ArH), 1375(vw, N—O), 1354(w, C—N), 1263, 1163, 1064(vs, C—O—C), 1199(s, $(CH_3)_2C{=}C$), 983(w, *trans*-H—C=N—R), 839, 804(w, 1, 4-Ar)cm^{-1}; MS (70 ev) *m*/*z* (%): 647(M+2, 0.11), 646(M+1, 0.39), 645(M+, 0.61), 627(0.58), 616(11.07), 615(25.79), 599(0.07), 573(0.49), 532(0.84), 532(0.84), 518(0.21), 492(0.15), 395(0.20), 365(3.13), 310(0.40), 282(0.12), 268(3.31), 252(9.67), 251(47.03), 211(8.74), 194(1.33), 178(0.99), 165(7.20), 140(14.25), 138(2.86), 124(100), 121(9.91), 107(4.43), 98(11.07), 93(1.63), 83(3.01), 65(1.78), 58(23.77), 55(4.36), 42(8.07).

3. Results and Discussion

3.1. Spectral Properties

The IR spectra of all the compounds show absorptions in the range of 1641–1643 cm^{-1}, which are assigned to the C=N stretching vibrations. Strong absorptions in the region of

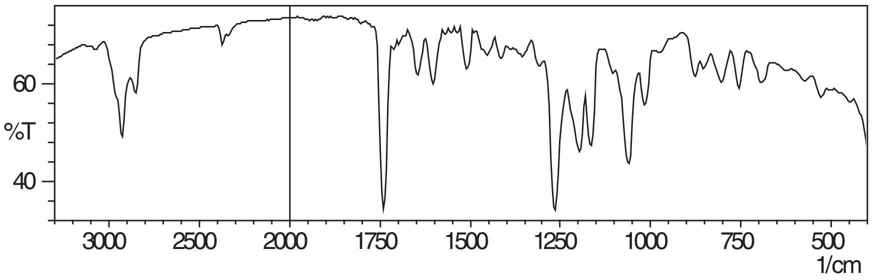


Figure 1. The IR spectrum of **7a**.

1737–1757 cm^{-1} for all the compounds are observed due to the presence of ester groups [16]. The N—O stretch is observed as a medium band in the region of 1373–1384 cm^{-1}[17]. The N—O (bending vibration) has been observed as split bands around 831–841 cm^{-1}[18]. The bending vibration of $=C(CH_3)_2$ is found at 1193–1199 cm^{-1}. The stretch of C—N of all compounds is observed at 1354–1364 cm^{-1}. The IR spectrum of representative compound has been shown in Fig. 1. The UV spectra of all the compounds in THF were measured in the region 200–500 nm. All the compounds show four absorption bands, one near 248 nm, the second near 253 nm, the third near 259 nm, and the last near 289 nm. The absorption near 289 nm is believed to be $\pi \rightarrow \pi^*$ of imino group (C=N) conjugated with the benzene system [19]. These representative compounds have been shown in Fig. 2.

3.2. Magnetic and Liquid Crystal Properties

The first sample that we began our study was **7f**, obtained from 4-(4-pentylphenyl) benzoic acid. DSC and POM measurement revealed that the liquid crystalline phase appeared between melting point 172.5°C and decomposing temperature 181.5°C, but a very viscous mesophase was observed (Table 1 and Fig. 3(d)). In order to reduce the viscosity and find the possibility to get a nemetic phase, an approach to replace the conjugated ring in the starting substrate by the corresponding saturated ring skeleton was tried and

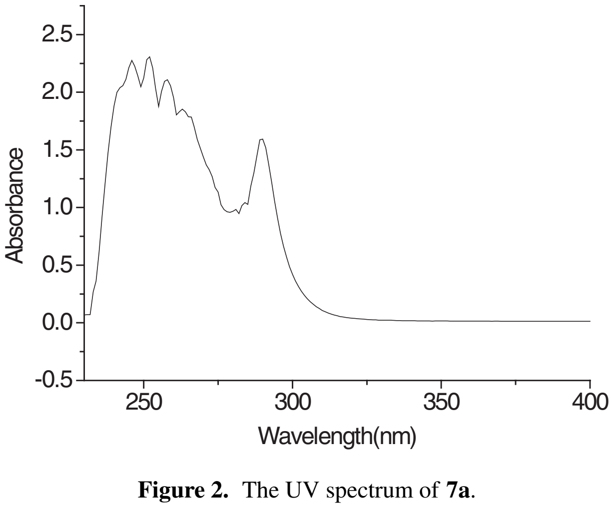
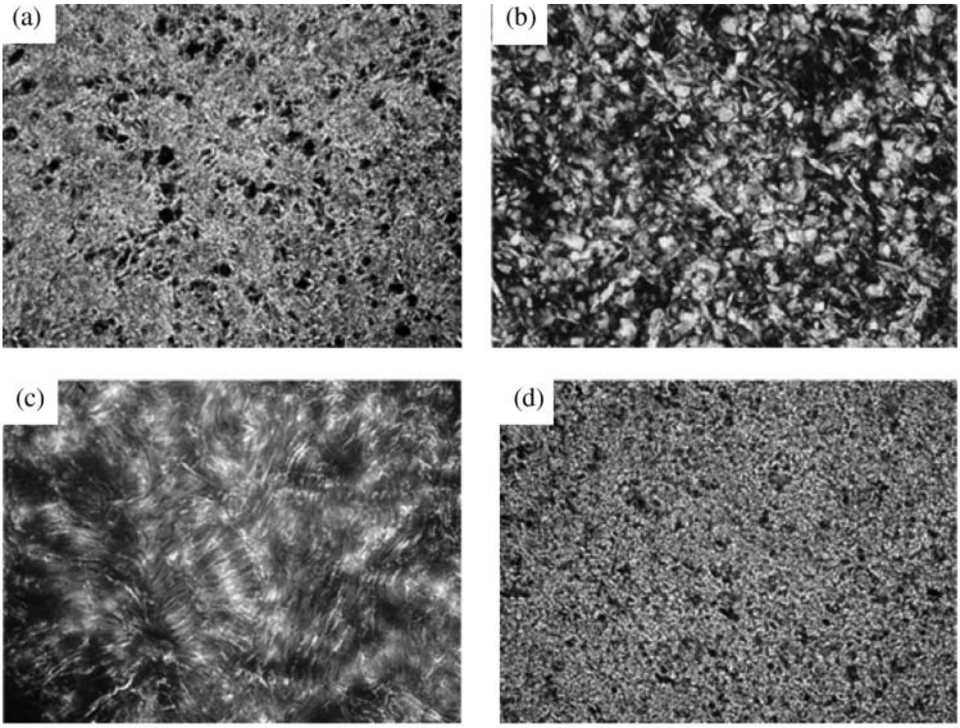


Figure 2. The UV spectrum of **7a**.

Table 1. The results of DSC measurement

Compd.	**7a**	**7b**	**7c**	**7d**	**7e**	**7f**
M.p.(°C)	170.7	160.5	157.6	172.3	177.5	172.5
ΔH of m.p. (kJ/mol)	8.42×10^{-5}	7.33×10^{-5}	7.37×10^{-5}	9.70×10^{-5}	7.61×10^{-5}	9.65×10^{-5}
C.p.(°C)	–	167.5	–	179.8	180.5	–
Range of meso phase(°C)	–	6.0	–	5.9	3.0	–
D.p.(°C)	188.2	185.6	171.2	181.7	183.6	181.5
ΔH of d.p. (kJ/mol)	-3.92×10^{-4}	-4.21×10^{-4}	-1.59×10^{-4}	-4.84×10^{-4}	-4.14×10^{-4}	-4.03×10^{-4}

Note: m.p. is melting point, c.p. is clearing point, d.p is decomposing point.



(a) The silk-like texture of **7a** taken at 177 °C ×300

(b) The schlieren texture of **7b** taken at 164.6°C ×300

(c) The silk-like texture of **7e** taken at 180.0°C ×300

(d) The silk-like texture of **7f** taken at 176.7°C ×300

Figure 3. The textures of some resulting compounds observed under polarizing optic microscope during heating process.

led to the compounds **7a**, **7b**, and **7e**, respectively. Measurements of compound **7a** also revealed the silk-like texture from melting temperature 170.7°C to decomposing temperature 188.2°C by DSC and POM (Table 1 and Fig. 3(a)). As expected, compounds **7b** and **7e** showed schlieren texture (Fig. 3(b)) and silk-like texture (Fig. 3(c)), respectively, which belong to the nematic phase. To further study, the influence of different ring A and B and terminal alkyl on this kind of molecule, the compounds **7c** and **7d** were also synthesized.

The compounds **7a**, **7b**, **7c**, **7d**, **7e**, and **7f** were measured by EPR spectroscopy and their g values were 2.0068, 2.0074, 2.0072, 2.0076, 2.0070, and 2.0075, respectively, just the same value as those of nitroxide free radicals [20].

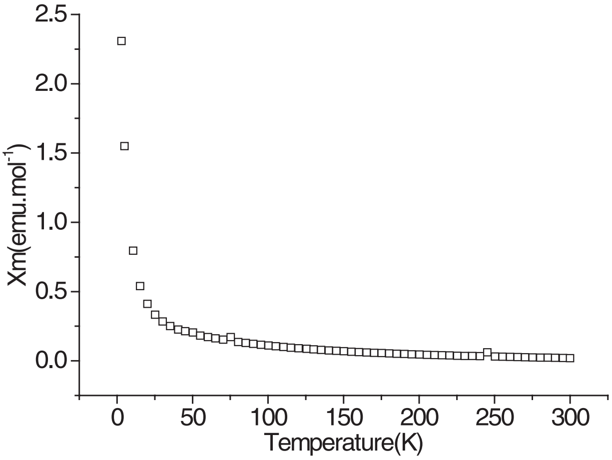


Figure 4. The Xm versus T plots of 7a.

Besides strength of magnetic field, the paramagnetism of any substances depends on temperature, whose susceptibility in inverse proportion to T. Figure 4 shows that in higher temperature areas, susceptibility of **7a** and T obeyed the Courier-Weiss law. Beyond 100 K, the compound is paramagnetic, while below 100 K, magnetism of compounds changes from paramagnetism to ferromagnetism, which departs the Courier-Weiss law and indicates magnetism adding. X_m^{-1} has better linear relationship with T (Fig. 5) during 135 K to 185 K with $r = 0.9991$, $C = 0.137$ emu K mol^{-1}, and $\theta = -5.54$ K. Our attempt to measure the diamagnetic susceptibility anisotropy of the compounds at nematic phase was not succeeded because at a temperature higher than 400 K, it was very difficult to control accurately the temperature between melting point and decomposing temperature. The decomposition occurred every time during several measurements.

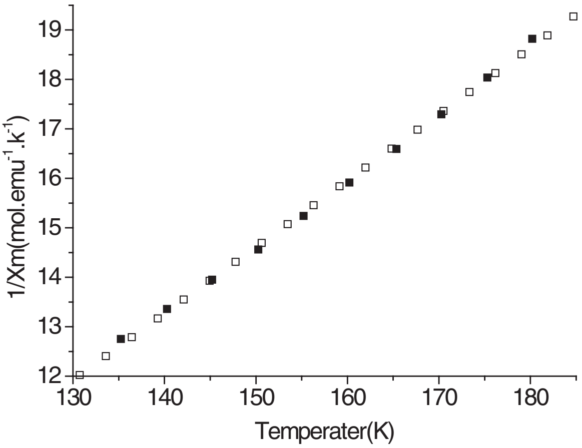


Figure 5. The 1/Xm.T versus T plots of **7a**. (The hollow dots are values of linear fitting.)

4. Conclusions

It has been shown that new rod-like magnetic liquid crystal molecules are successfully synthesized by a combination of long rigid core with bulky TEMPO as a terminal unit. Further, modification of the molecular structure allows the molecules to exhibit a phase behavior belong to the nematic phase, which provides an opportunity to investigate their thermomagnetic properties and to be used as a dopant in liquid crystal mixture. Because such kind of magnetic compounds all decompose at the temperature around 200°C, it is difficult to widen their temperature ranges of mesophase.

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