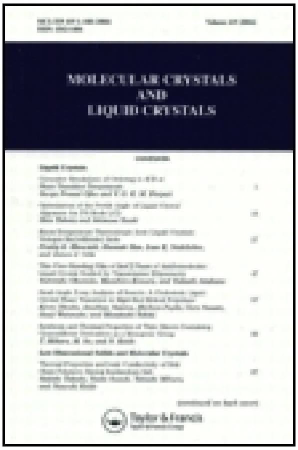

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Nematic Liquid Crystal Containing Diaza-18-Crown Ether Unit

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Nematic Liquid Crystal Containing Diaza-18-Crown Ether Unit

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Three diaza-18-crown-6 carrying aryl ester structural unit were synthesized and shown to nematic liquid crystalline properties. The influence of the molecular structure on liquid crystalline properties was studied. It has been found that whether the complexes display liquid crystalline properties depends upon structure of anions. The influence of doping inorganic salt on the clear point was also studied.

Keywords: nematic liquid crystal, crown ether, doping

If crown ether compounds have mesomorphic properties, it may cause some special effects. In addition to changing the electro-optic effect, magnetic effect, and photovoltaic effect etc., they have the ability of coordination with metal ions. These new physical properties will further enrich physics, organic chemistry, bionics, and molecular engineering etc. Because crown ethers can complex metal ions, the conductance of liquid crystal can be improved, and the threshold value of electric current and voltage will be reduced. The lower threshold value, responding faster display liquid crystal and colour liquid crystal which may be achieved by mesomorphic crown ethers coordinating with different metal ions, even colour anions, will be obtained. Maybe the mesomorphic crown ethers will be applied to separating metal ions with membrance. As the features of mesomorphic crown ethers are realized, it is certain that varieties of their applications will be developed.

Since cholesterol mesomorphic crown ethers had first been reported by L. G. Bogatskaya *et al.*[1] in 1982, nematic,[2–6] dish,[7–8] polymer[9–12] mesomorphic crown ethers were reported one after another. However, all in all, the researches of them were a trial. The researches, over which we took a general view, had some questions as follows:

1. What structure needed crown ethers to exhibit mesomorphic state?
2. What differences had crown ethers liquid crystal from others in structure?
3. The properties of mesomorphic crown ethers, and what characteristics their

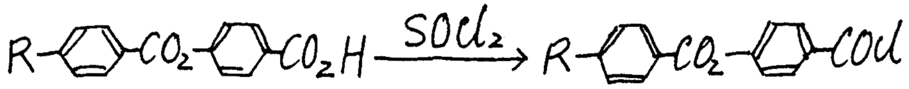
coordination compounds possess in mesomorphic phase, had not been reported.

4. The applications of them had not been reported also.

Starting with the existing questions in the investigations of mesomorphic crown ethers, our works were focused as follows:

On the basis of structure characteristic for general nematic liquid crystals, which L/D ratio is usually 4 ~ 8, some mesomorphic crown ethers containing diaza-18-crown-6-ether which had been reported and were designed by us were estimated with CPK (Corey-Pauling-Koltun) atomic model. The L/D ratio of them were obtained, so that the synthesis were guided in theory. It was hoped that target molecules were nematic, and the relations between the structure and the properties were found out. It was also hoped that some condition, under which coordination compounds of mesomorphic crown ethers displayed mesomorphic state, were found out.

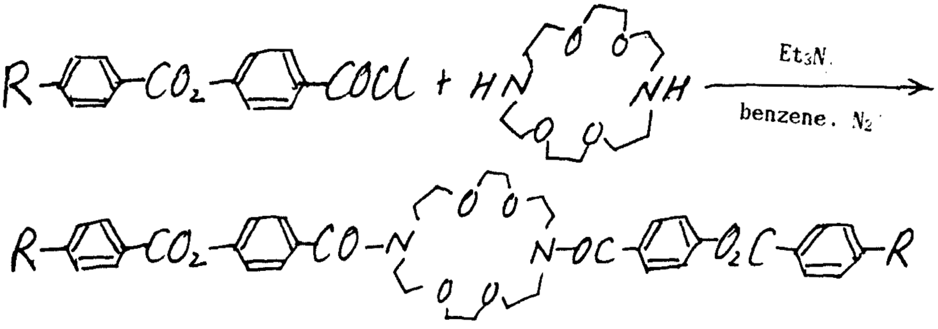
Scheme of synthesis:



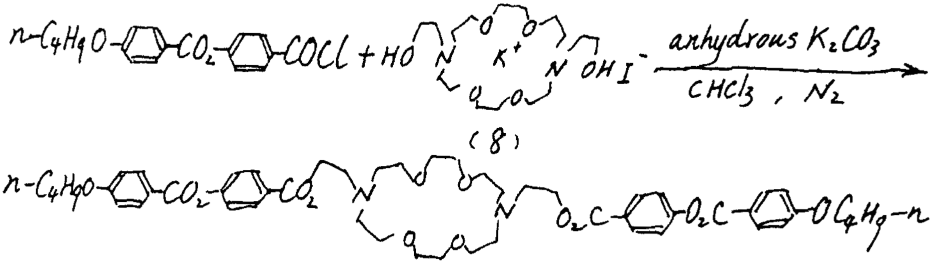
(1) $R = n\text{-}C_5H_{11}$ (4) $R = n\text{-}C_5H_{11}$

(2) $R = n\text{-}C_7H_{15}O$ (5) $R = n\text{-}C_7H_{15}O$

(3) $R = n\text{-}C_4H_9O$ (6) $R = n\text{-}C_4H_9O$



(9) $R = n\text{-}C_5H_{11}$ (10) $R = n\text{-}C_7H_{15}O$



(11)

RESULTS AND DISCUSSIONS

The Synthesis Concerning Nematic Crown Ethers

The ester type liquid crystals are generally white, no toxicity, more stable toward the action of water, light and oxygen than azo and Schiffs base. Their transition temperatures are lower and wider in nematic phase. The other physical properties can be improved by changing the situation and polar of side chain substituted group in benzene ring, thus their applications are expanded. We tried to join nematic molecules to crown ethers, to hopefully improve their electric conductivity and remain nematic properties to ester.

Compounds **(9)**, **(10)** and **(11)** are three diaza-18-crown-6-ethers carrying aryl ester unit. The results which were obtained with DSC show that they display mesomorphic properties (Figures 1–3). By relying on the texture which were taken (Figures 4–6), because the multiple linear grain appears in the texture, which has the characteristic of nematic phase, they are nematic liquid crystals.

The theory of the molecular structure for nematic liquid crystal[15] is that the L/D ratio of nematic liquid crystal must be bigger than four.

When we designed and synthesized these mesomorphic crown ethers, the L/D ratio of target molecule were estimated with CPK atomic model (Table I). We expect that the target molecules would theoretically be nematics when the L/D ratio was bigger than four, as was consistent with our experimental results. This indicated that the present theory of the molecular structure for nematic liquid crystal had instructive significance in synthesizing nematic liquid crystals containing diaza-18-crown-6 unit.

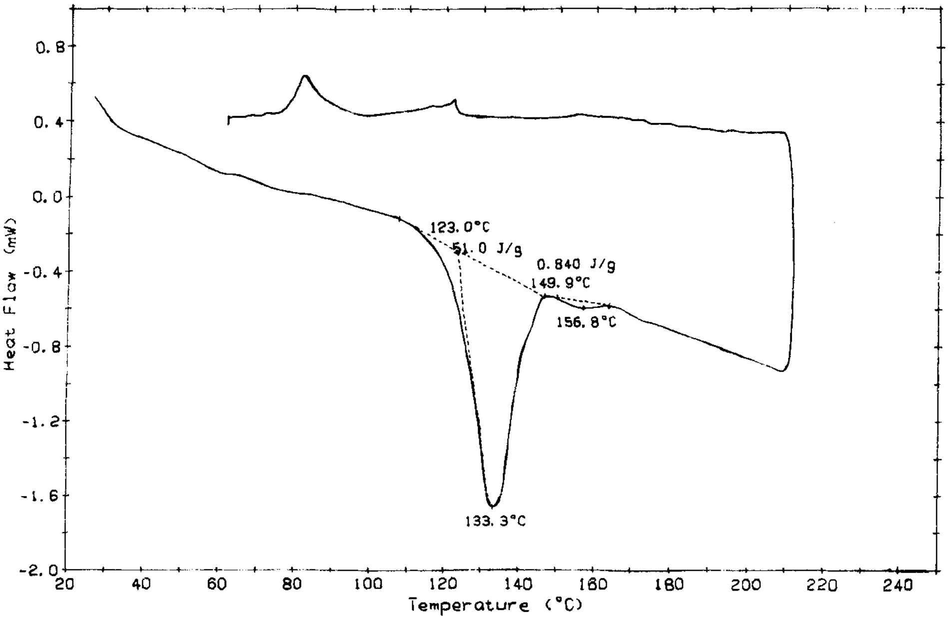


FIGURE 1 DSC of Compound **(9)**.

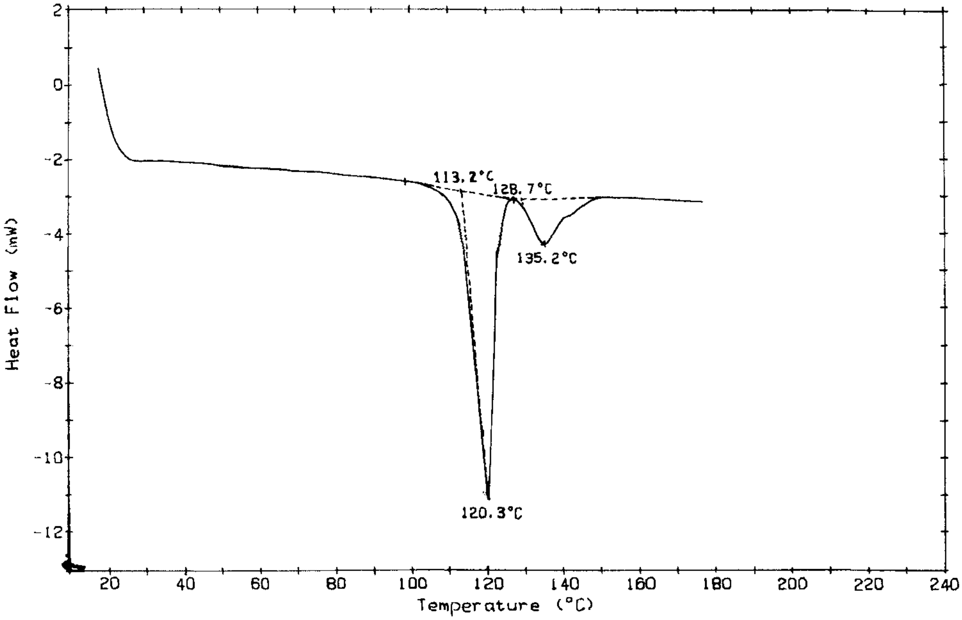


FIGURE 2 DSC of Compound (**10**).

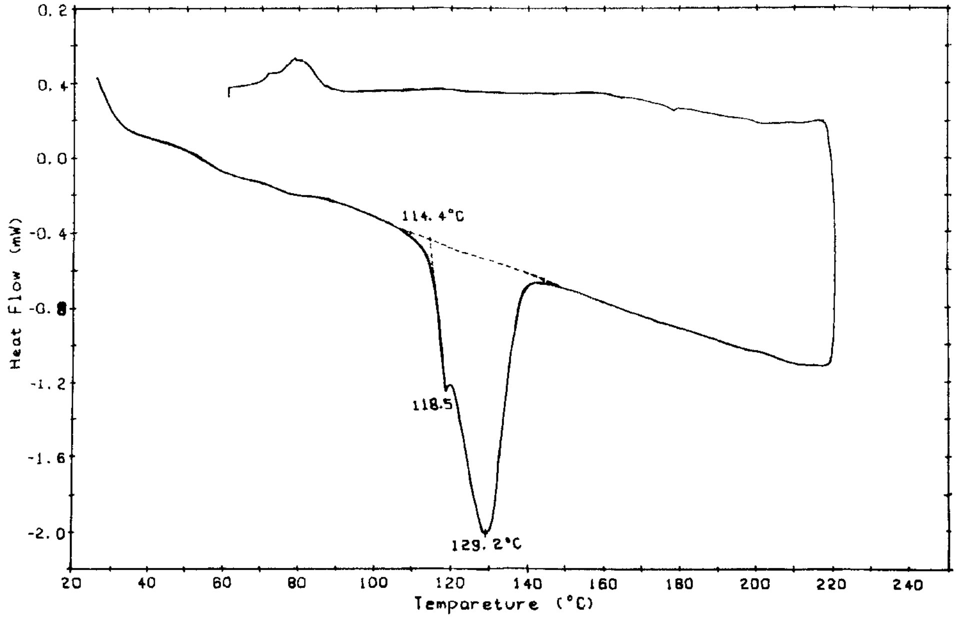


FIGURE 3 DSC of Compound (**11**).

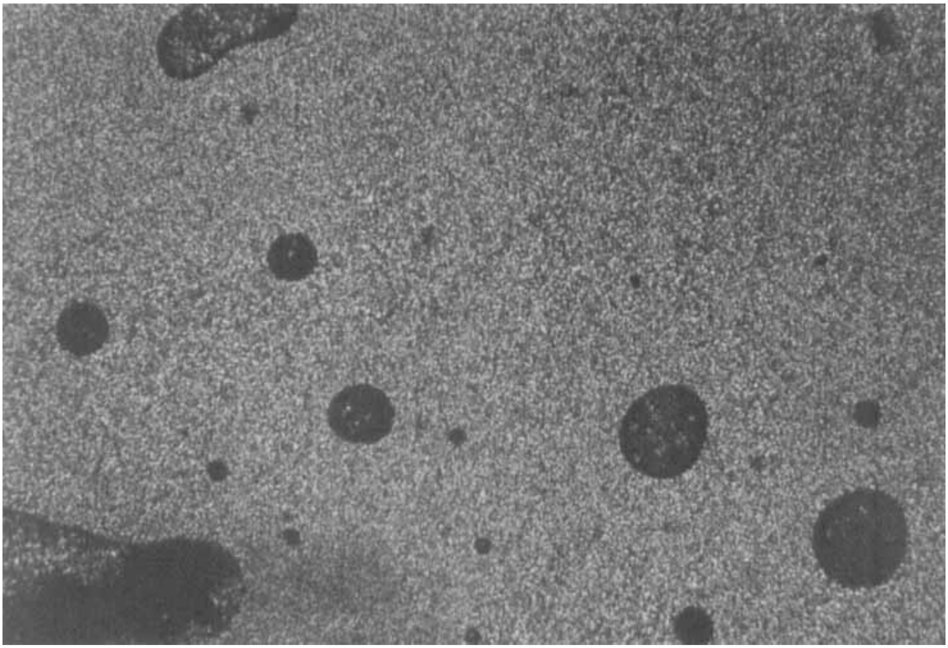
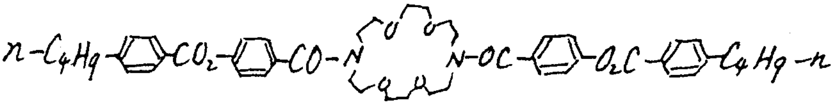


FIGURE 4 Texture of Compound (**9**) (temp. 142°C). See Color Plate IX.

The Structure of Compound (**12**) as follows:



It is seen from Table I that the melting point decreases with increasing the molecular length. The reason is that the molecular symmetry reduces as alkyl chain increases. The nematic range of compound (**11**) is narrower, because the ethylene between diaza-18-crown-6-ether and 4-(4′-butyloxybenzoloxy) benzoloxy makes molecular rigidity reduce. When the compound (**11**) was designed, the ethylene was joined so that the acylamide compound was changed into the ester type tertiary amine, in order to make the melting point lower. The result show, though the melting point reduces somewhat, the nematic range is narrower.

The Properties of Liquid Crystal Crown Ethers

Using conductance method, at 25 ± 0.01°C, in MeCN-$CHCl_3$ solution (2:3), the coordinate constants of the compounds (**9**), (**10**) with $KClO_4$ were determined. The constants (log K) are 7.94 and 7.70, respectively.

Some structural variation on crown ethers can result in mesomorphic property. After they formed coordination compounds, whether or not they were derived to possess mesomorphic property, which had not been answered. Thus, by doping metal salt in the compound (**10**), the properties of the coordination compound of

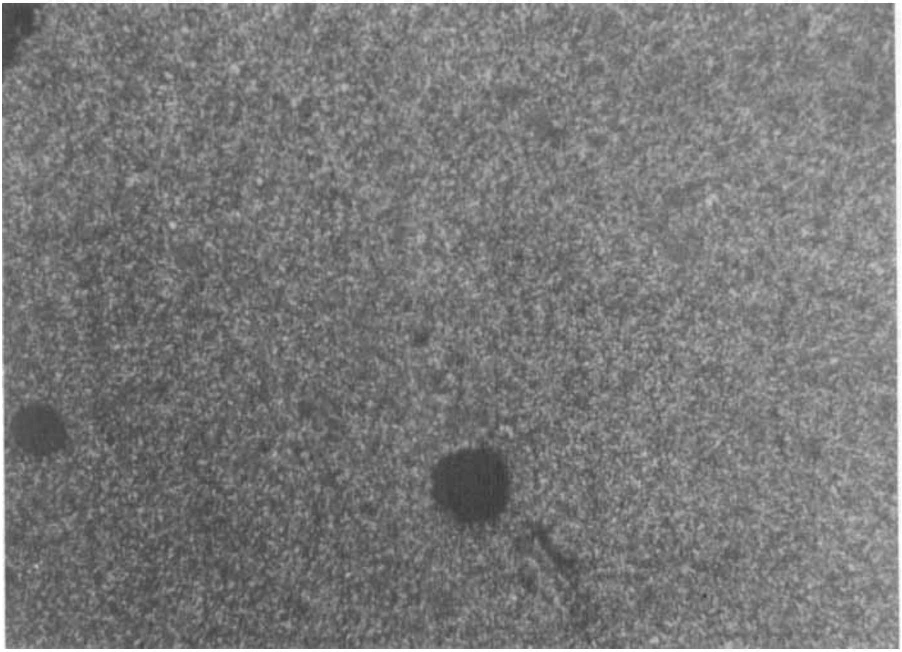


FIGURE 5 Texture of Compound **(10)** (temp. 129°C). See Color Plate X.

crown ether and the influences of content and assortment of dopant on mesomorphic property were realized.

Doping method is that some metal salt and nematic crown ether **(10)** are dissolved in acetone (or chloroform, methanol). At room temperture, the solvent is evaporated at reduced pressure, and the residue is melted, cooled. The doping nematic crown ethers were obtained, they were measured with DSC, the results were given in Figure 7 and Table II.

Because of solubility, the only seven doping compounds in Table II were done. We may see in Figure 7 as the doping content of KSCN increases, the clear point of doping liquid crystal decreases.

The results in Table II show, in all dopants of potassium salts being doped in compound **(10)**, only the dopants of KSCN and potassium picrate display nematic phase. Each of dopants of thiocyanate has nematic property. It indicates that after mesomorphic crown ethers form coordination compounds, which coordination compounds have mesomorphic property or not depends on coordinate anion, but not cation type.

The explanation of above-mentioned results is, the nematic crown ether as ligand reacts with doping metal salt forming coordination compound. After crown ether complexes metal ion, the complex compound is order or not, which depends on whether the crown ether is order or not.

On nematic crown ethers, whether or not their coordination compounds of metal

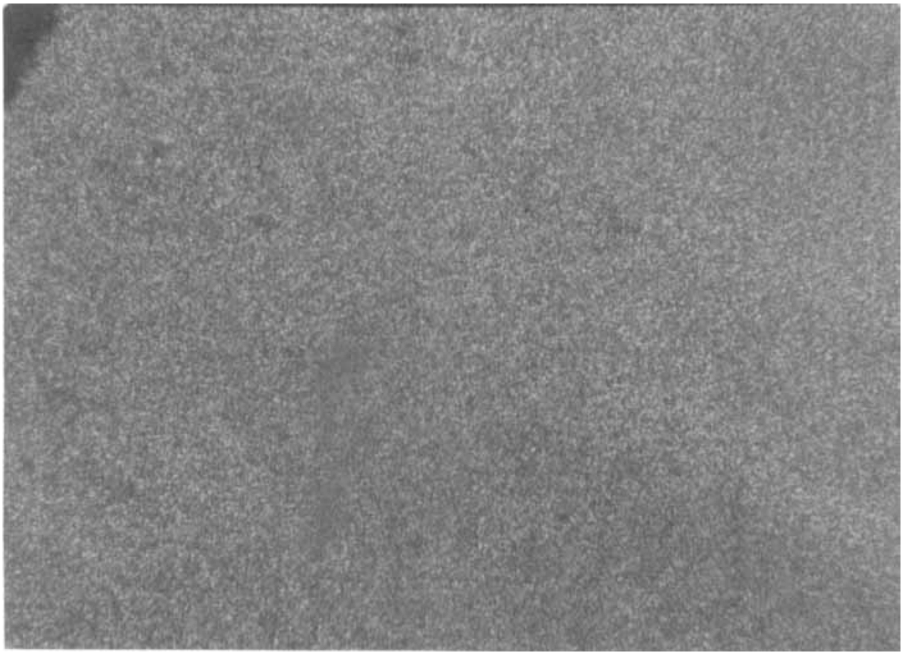


FIGURE 6 Texture of Compound (**11**) (temp. 124°C). See Color Plate XI.

TABLE I

The relation between the L/D ratio of mesomorphic crown ethers and transition temperature

Compound	L/D Ratio	T_{KN} (°C)	T_{NI} (°C)
12[2]	4.17:1	153.8	218
9	4.3 :1	133.3	156.8
10	5.0 :1	120.2	135.2
11	5.3 :1	118.5	129.2

salts have nematic property depends on anion. It is reasonable that structure of anions forming coordination compounds is different, halogen anion and ClO_4^- are spherical or close to spherical, SCN^- is linear, and picrate anion is plate. No matter how big spherical anion is, its orientation is isotropy. When it forms the coordination compound of mesomorphic crown ether, the order of the coordination compound reduces in liquid state so that its nematic phase disappears. The order of linear and plate anion is anisotropy. The doped coordination compound remains order in liquid phase, so it still has mesomorphic property.

The above-mentioned results obtained are useful for preparing the coordination compound of mesomorphic crown ethers and developing the electroconducting liquid crystal. If selecting cation of metal salt is transition metal ion, and anion is

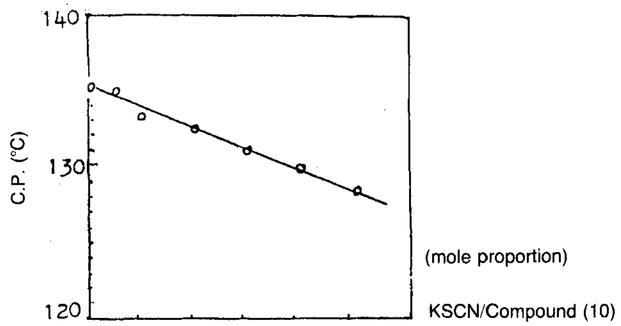


FIGURE 7 The effect of the content of doping KSCN in compound (**10**) on the clear point (CP).

TABLE II

The melting point and clear point of the dopants of metal salts and compound (**10**) (mol ratio 1:1)

Dopant	KCl	KI	$KClO_4$	Potassium picrate	KSCN	NH_4SCN	NaSCN
mp (°C)	127-9	124-5	125.5-8	115	120.2	119	118.5
CP (°C)	—	—	—	125	128.7	130.3	129.5

linear or plate, the coordination compound of mesomorphic crown ether with the salt forming a kind of new colour electroconducting liquid crystal will be developed.

EXPERIMENTAL

Infrared (IR) spectra were recorded (FT-IR 170 SX) as neat films on KBr plates. Proton nuclear magnetic resonance (^{1}H-NMR) were recorded on JNM-FX 90 Q spectrometer in $CDCl_3$ solvent. Mass spectrometry (MS) were carried out on Finnigan-Mat 4510 GS-MS and Hitach M-80 A GS-MS(FD). Element analysis were obtained on CARLO ERBA 1106. Differential scanning calorimeter (DSC) were recorded on Dupont 1090 Thermal Analysis. Textures were taken on XPT-7 Microscope with Polariscope (Attachment is a heat plate which was produced by Scientific Instrument Plate of Sichuan University).

The Synthesis of Intermediate and Products

The intermediates (1, 2 and 3): 4-alkyl (or alkyloxy) benzoic acid and thionylchloride are mixed in benzene. The resulting solution is refluxed for 10 hrs. The benzene and the excess of thionylchloride is removed by distillation. The corresponding chloride are obtained. To a solution of p-hydroxy benzoic acid in dried pyridine, these chlorides are respectively added. The mixture is stirred at room temperature for 24 hrs and is then acidified with 10% hydrochloric acid (pH ≈ 1). The resulting precipitate of ester is filtered off, washed with water. Recrystallization from ethanol afford the desired white products about 55% yield. (**1**): T_{KN} 152°C, T_{NI} 272°C,

$C_{19}H_{20}O_4$ (Calcd. for C, 73.08, H, 6.41%; Found: C, 72.60, H, 6.27%). ν_{max}: 3300–2500 (br. OH), 1736, 1692 (S, ArC=O), 1604, 1508 (S, Ar), 1288, 1208, 1181 (S, Ar—O—C) cm^{-1}. δ_H: 0.91 (3H, *t*, CH_3), 1.16–1.88 (6H, *m*, $3XCH_2$), 2.71 (2H, *t*, $ArCH_2$), 7.12–8.36 (8H, *m*, 2 × $[Ar\text{-}H]_4$) ppm. m/z: 313 ($[M + H]^+$, 1%), 295 ($[M - OH]^+$, 4), 175 ($[C_5H_{11}C_6H_4CO]^+$, bp). **(2)** T_{KN} 152°C, T_{NI} 240°C, $C_{21}H_{24}O_5$ (Calcd. for C, 70.79, H, 6.74%; Found: C, 70.40, H, 6.90%). ν_{max}: 3000–2500 (br. OH), 1734, 1681 (S, ArC=O), 1608, 1510 (S, Ar), 1253, 1212, 1160, 1070 (S, Ar—O—C) cm^{-1}. δ_H: 0.91 (3H, *t*, CH_3), 1.12–1.95 (10H, *m*, 5 × CH_2), 4.14 (2H, *t*, $ArOCH_2$), 7.00–8.24 (8H, *m*, 2 × $[Ar\text{-}H]_4$) ppm. m/z: 357 ($[M + H]^+$, 4%), 339 ($[M - OH]^+$, 18), 219 ($[C_7H_{15}C_6H_4CO]^+$, bp). 121 ($[HOOCC_6H_4]^+$, 45). **(3)** T_{KN} 177°C, T_{NI} 256°C, $C_{18}H_{18}O_5$ (Calcd. for C, 68.79, H, 5.73%; Found: C, 68.57, H, 5.50%). ν_{max}: 3300–2500 (br. OH), 1728, 1698 (S, ArC=O), 1604, 1511 (S, Ar), 1260, 1208, 1160 (S, Ar—O—C) cm^{-1}. δ_H: 1.00 (3H, *t*, CH_3), 1.18–2.00 (4H, *m*, 2 × CH_2), 4.07 (2H, *t*, $ArOCH_2$), 6.88–8.28 (8H, *m*, 2 × $[Ar\text{-}H]_4$) ppm. m/z: 315 ($[M + H]^+$, 2%), 297 ($[M - OH]^+$, 10), 177 ($[C_4H_9OC_6H_4CO]^+$, bp), 121 ($[HOOCC_6H_4]^+$, 50).

The intermediates (**7** and **8**) are obtained respectively, by the method of Kulstad[13] and Xie[14], (**7**) mp. 113–4°C (lit[13] 114–5°C), (**8**) mp. 182–4°C (lit[14] 182–3°C).

The product (**9**): compound (**1**) (10.8 mmol) is refluxed in thionylchloride for 10 hrs. The compound (**4**) is obtained by distillation at reduced pressure, and then dry benzene (20 ml) is added to the residue. Under the protection of nitrogen gas, a solution of compound (**7**) (1.31 g, 5 mmol) in dry benzene (30 ml) and triethylamine (3.2 ml) is added dropwise. The resulting mixture is refluxed for 17 hrs, and then cooled. The precipitate of triethylamine chloride is filtered off. The filtrate is distilled, at reduced pressure, to remove the benzene. The resulting solid residue is taken up in chloroform and washed with water three times. The organic layer is distilled, at reduced pressure, to remove chloroform. The resulting residue is recrystallized several times from ethanol until the transition temperatures are constant. The product is white powder crystal. Yield: 75%, T_{KN} 133.3°C, T_{NI} 156.8°C, $C_{50}H_{62}N_2O_{10}$ (Calcd. for C, 70.51, H, 7.29%, N, 3.29; Found: C, 70.25, H, 6.81%, N, 2.85). ν_{max}: 1737 (S, ArC=O), 1622, 1510 (S-m, Ar), 1269, 1127, 1044 (S, Ar—O—C, C—O—C) cm^{-1}. δ_H: 0.90 (6H, *t*, 2 × CH_3), 1.20–1.85 (12H, *m*, 2 × $[CH_2]_3$), 2.71 (4H, *t*, 2 × $ArCH_2$), 3.62 (16H, S, 8 × CH_2O), 3.80 (8H, S, $4[Ar\text{-}H]_4$) ppm. m/z (FDMS): 851 ($[M + H]^+$, 6%), 677 (11), 310 (8), 175 ($[C_5H_{11}C_6H_4]^+$ CO, bp).

The product (**10**) is prepared by means of product (**9**). It is white powder crystal. T_{KN} 120.2°C, T_{NI} 135.2°C, $C_{54}H_{70}N_2O_{12}$ (Calcd. for C, 69.08, H, 7.46, N, 2.98%, Found: C, 68.65, H, 7.34, N, 2.88%). ν_{max}: 1732 (S, ArC=O), 1616, 1514 (S, Ar), 1266, 1167, 1072 (S, Ar—O—C, C—O—C) cm^{-1}. δ_H: 0.90 (6H, *t*, 2 × CH_3), 1.18–2.04 (2OH, *m*, 2 × $[CH_2]_5$), 3.62 (16H, S, 8 × CH_2O), 3.62 (16H, S, 8 × CH_2O), 3.78 (8H, S, 4 × CH_2N), 4.04 (4H, *t*, 2 × CH_2OAr), 6.82–8.20 (16H, *m*, 4 × $[Ar\text{-}H]_4$) ppm. m/z (FDMS): 938 (M^+, 12%), 439 (12), 437 (bp), 395 (18).

The product (**11**): compound (**3**) (6.4 mmol, 2g) is refluxed in thionyl-chloride for 10 hrs. The compound (**6**) is obtained by distillation at reduced pressure, and then chloroform (30 ml) and anhydrous K_2CO_3 (4.4 g) are added to the residue. Under the protection of nitrogen gas, the compound (**8**) (3.2 mmol, 1.65 g) dissolved in 20 ml of chloroform, is added dropwise. The resulting mixture is refluxed for 48 hrs, and then cooled. The inorganic solids are filtered off. The filtrate is washed with water and distilled, at reduced pressure, to remove chloroform. The resulting solid residue is recrystallized from ethanol several times until the transition temperature remain constant giving white powder product. Yield: 68%, T_{KN} 118.5°C, T_{NI} 129°C, $C_{52}H_{66}N_2O_{14}$ (Calcd. for C, 66.24, H, 7.01, N, 2.97%; Found: C, 65.94, H, 6.91, N, 2.81%). ν_{max}: 1729 (S, ArC=O), 1606, 1510 (S, Ar), 1277, 1127, 1069 (S, Ar—O—C, C—O—C) cm^{-1}. δ_H: 0.97 (6H, *t*, 2 × CH_3), 1.22–1.92 (8H, *m*, 2 × $[CH_2]_2$), 3.00 (12H, S, 6 × CH_2N), 3.63 (16H, S, 8 × CH_2O), 4.06 (4H, *t*, 2 × CH_2OAr), 4.45 (4H, *t*, 2 × CH_2OCO), 6.86–8.20 (16H, *m*, 4 × $[Ar\text{-}H]_4$) ppm. m/z (FDMS): 944 ($[M + 2H]^+$, 70%), 942 (M^+, 22), 630 (bp).

Acknowledgment

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References

1. L. G. Bogatskaya, N. G. Lukyanenko, E. Yu. Kulygine and N. L. Nesterenko, Ninth International Conference on Liquid Crystals. Programme and Abstracts, Bangalore, 1982, p. 15.
2. M. G. Xie, S. Huang and L. Y. Wang, Third National Conference on Crownether Chemistry of China, Vol. 1, Tai Chang, China (1984).
3. Ю. С. Липатов, В. В. Цукрук, В. В. Щилов, В. Н. Пастушок, А. И. Галатина, А. В. Богатский, Докл. Акад. Наук., С. С. С. Р, 1985, 285(1), 155(Физ. Хим.).
4. Shinkai Seiji, Jpn. Kokai Tokkyo Koho JP87 74.
5. B. Z. Tian and S. Huang, 4th National Conference on Cronwether Chemistry of China, Chengdu, China, 1987, p. 37.
6. G. X. He, F. Wada, K. Kikukawa and T. Matsuda, J. C. S. Chem. Commun., 1987, 1287.
7. J. M. Lehn, J. Malthete and A. M. Levelut, J. C. S. Chem. Commun., 1985, 1794.
8. C. Mertesdorf and H. Ringsdorf. Twelfth International Conference on Liquid Crystals. Programme and Abstracts, 1988, p. 151.
9. V. Percec and R. Rodenhouse, Polym. Prepr., 1988, 29(2), 196.
10. В. В. Зуев, М. С. Романова, С. С. Скороходов, М. М. Когон, Высокомодек. Соед. Б, 1988, 30(8), 610.
11. J. M. G. Cowie and H. H. Wu. British Polym. J., 1988, 20(6), 515.
12. V. Perce and R. Rodenhouse, Macromolecules, 1989, 22(5), 2043.
13. S. Kulstad and L. A. Malmsten, Acta Chem. Scand., 1979, Ser. B., B33, 469.
14. M. G. Xie, and J. P. Li, 4th National Conference on Cronwether Chemistry of China, Chengdu, China, 1987, p. 39.
15. G. H. Brown and J. J. Wolken, "Liquid Crystals and Biological Structures," Academic Press, 1979, p. 21.