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STRUCTURES AND MESOMORPHIC PROPERTIES OF CROWN ETHER LIQUID CRYSTALS

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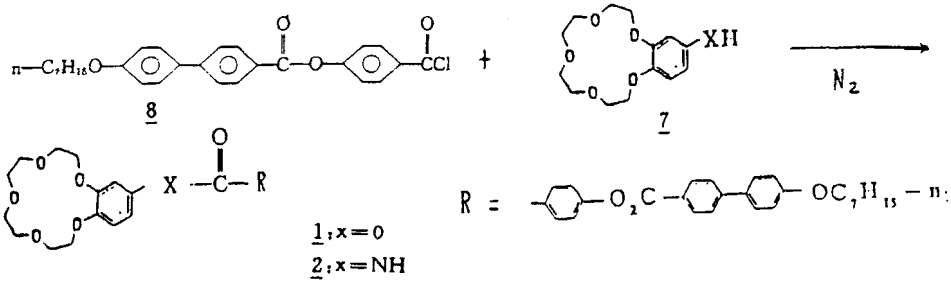
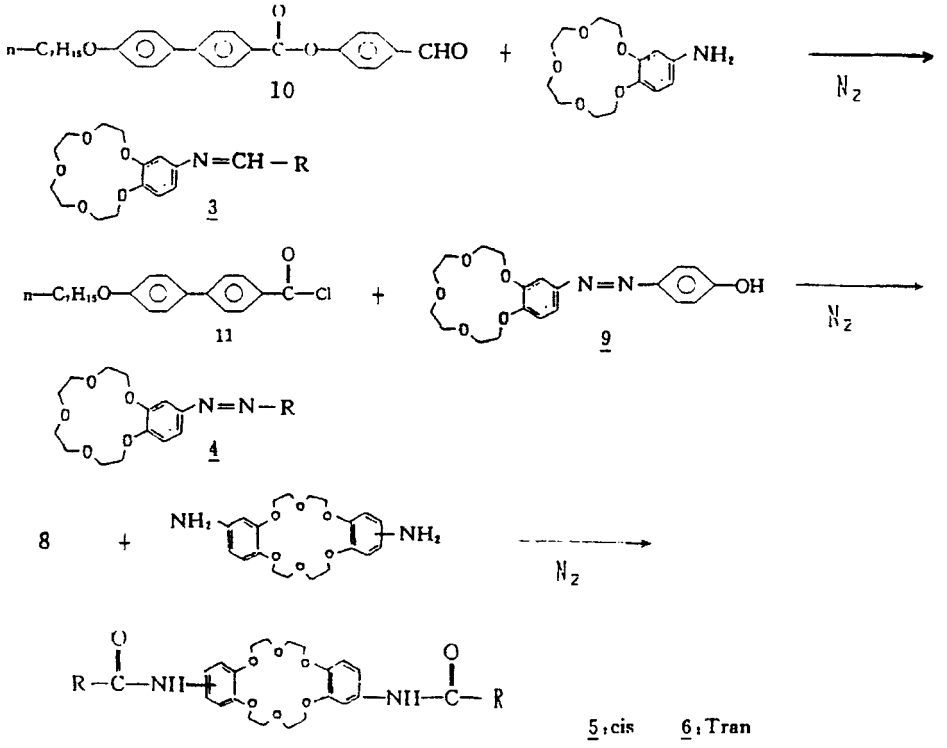
Abstract Six crown ether liquid crystals have been designed and synthesized. Their chemical structures have been elucidated by Elementary Analysis, IR, ^{1}HNMR, and MS. Their mesomorphic properties were determined by using DSC and textures. The relationship between the structures of crown ethers and the mesomorphic properties were studied.

Key words: Crown ether liquid crystals, mesomorphic properties, chemical structures.

INTRODUCTION

Crown ether liquid crystals, which possess the properties of both crown ethers and liquid crystals, have attracted extensive attentions since they were first reported in 1982. The relationship between the structures of crown ethers and the mesomorphic properties is the focus. In this paper six crown ether liquid crystals have been designed and synthesized based on our previous work. The relationship of crown ethers and mesomorphic properties have been studied.





RESULTS AND DISCUSSION

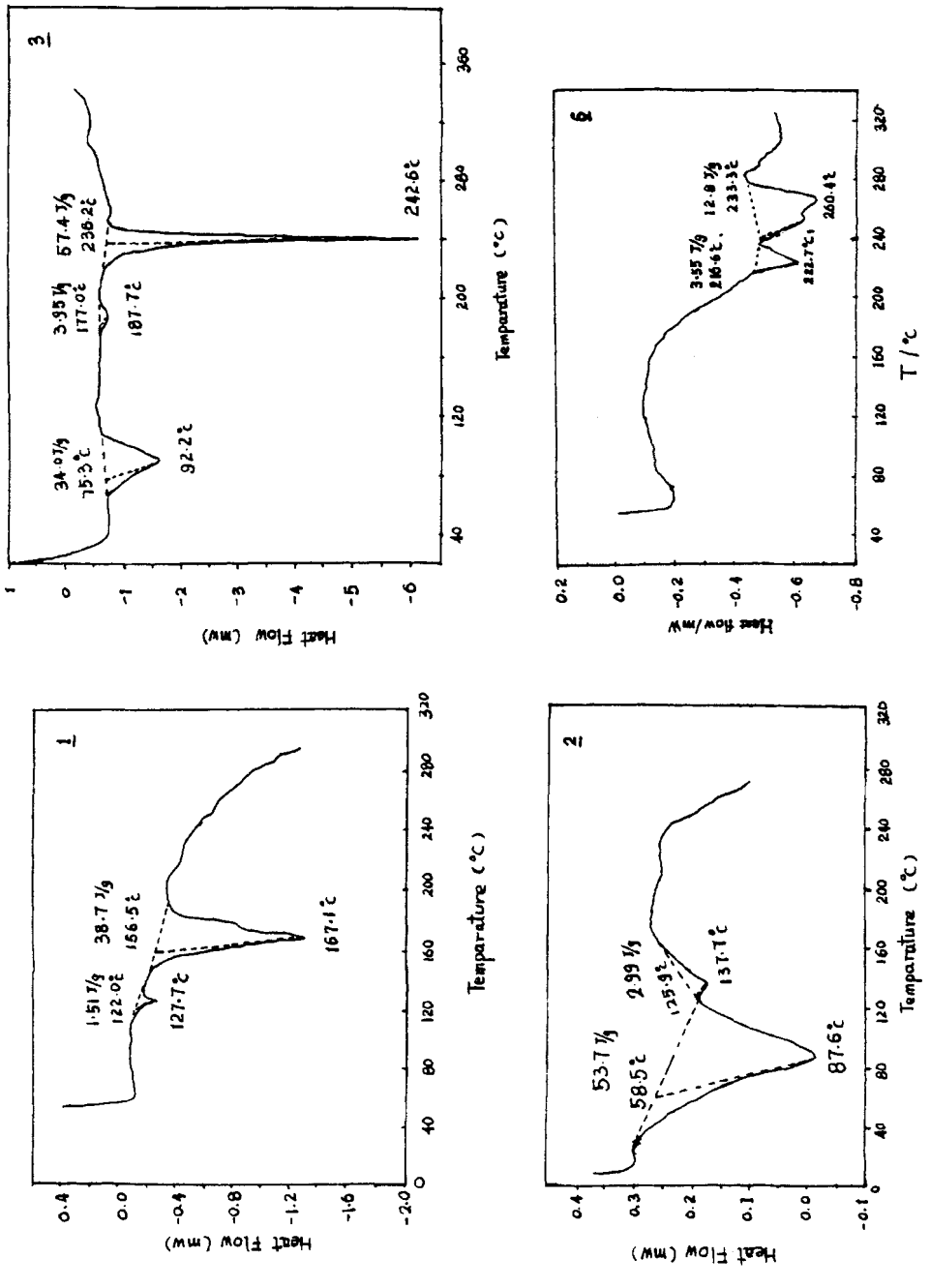
According to CPK molecule model, all the six compounds, with L/D values between 3 and 8, have good planility and proper hardness and polarity, which means they have mesomorphic properties. Mesomorphic properties were determined by DSC analysis (Fig. 1)

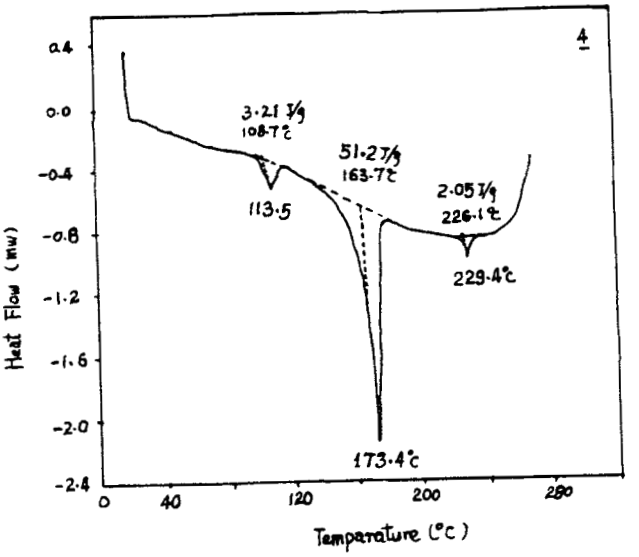
The phase transition temperatues of disubstrituted amide crown ethers 5 and 6 are far more higher than monosubstituted one 2.

It is the crown ether rings but not bridge bonds in the substitute arms that has influence on the phase transition points of the compounds.

In monosubstituted crown ethers, the bridge bonds have big influence on thermal stability of crown ether liquid crystals. The order of mesomorphic clear

Fig1 The DSC of Compounds





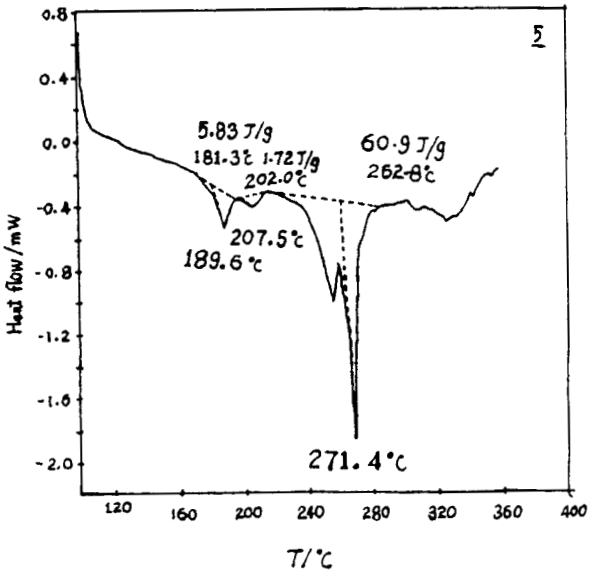
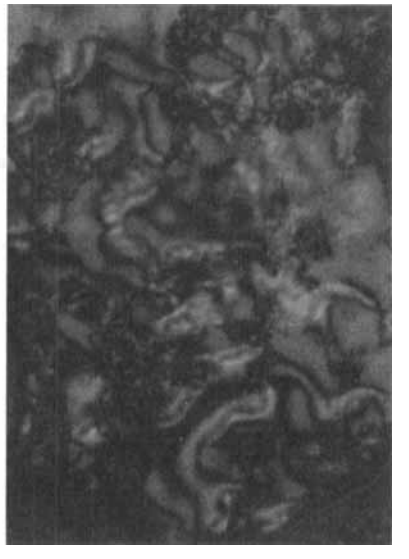


Fig2 The Texture of Compounds (See Color Plate VII).

Compound 1 on heating 164℃

Compound 2 on cooling 118℃

Compound 3 on coolong 156℃



Compound 4 on heating 208℃

points of different compounds is as follows: -N=CH->-N=N->-O-$\overset{\overset{O}{\|}}{C}$->-NH-$\overset{\overset{O}{\|}}{C}$—. In monosubstituted schiff base and azo crown ethers, because of the existance of carbon-nitro and carbon-carbon double bonds, delocalized conjugated π bonds were formed among π electrons of double bonds, phenyls in benzo crown ether rings and aryls in substitute arms. In ester and amide crown ethers, because p-π conjugation, that is weaker than π-π conjugation, was formed, the clear points were decreased.

The smectic or nematic phases appeared in liquid crystal crown ethers were determined by terminal or lateral intermolecular attraction strength.

In monosubstituted liquid crystal crown ethers, because the polar crown ether rings were at the end of the molecular chains, which increased the terminal intermolecular attraction, nematic phases could appear. That is consistent with textures (Fig. 2). But in compounds 3 and 4, delocalized big π bonds increased the lateral intermolecular attraction, so smectic phase were observed. A curve-shaped cis-disubstituted amide crown ether increased the lateral intermolecular attraction, so smectic phases were observed.

With the increasing temperatures, the entropy of the system and the degree of discorder were increased, and, at last, the disordered state was reached. Two phases are equilibrium at the phase transition point. The relationship of ΔS and ΔH are shown as follows.

$$\Delta S = \Delta H / T$$

The ΔS values of compounds 1~6 at the transition points are list in Tab. 1

Table 1 Thermodynamic Data of Crown Ether Liquid Crystals

Compound	M	Phases	Transition Point K	ΔH(KJ/mol)	ΔS'(J/mol · k)
1	698	K→N	400.9	1.05	2.62
		N→I	440.9	27.0	61.32
2	697	K→N	360.8	37.4	103.66
		N→I	410.9	2.08	5.06
3	681	K→S	365.4	23.2	63.49
		S→N	460.9	2.69	5.84
		N→I	515.8	39.1	75.80
4	682	K→S	386.7	3.09	7.99
		S→N	446.6	34.9	78.5
		N→I	502.6	1.4	2.79
5	1218	K→S	461.8	7.1	15.38
		S→N	470.7	2.09	4.45
		N→I	544.6	74.2	136.2
6	1218	K→N	495.9	4.3	8.72
		N→I	539.6	15.6	28.89

According to Fig. 1 and Tab. 1, the ΔS values of liquid crystal crown ethers are contrary to usual nematic liquid crystals. Some liquid crystal crown ethers have $\Delta S_{KN} > \Delta S_{NI}$ and low vicidity in nematic phases. Some liquid crystal crown ethers have $\Delta S_{KN} < \Delta S_{NI}$ and high vicidity in nematic phases. The polar crown ether rings increased the intermolecular attraction and vidicity of mesomorphases.

EXPERIMENTAL

Instruments

IR: Nicolet FT-IR 170SX Infared spectrometer

^{1}HNMR: JNM-FX 90Q NMR Spectrometer

MS: Finnigan-Mat 4510 (EI) GS-MS

Elementary Analysis: Carlo Erba 1106

DSC: Du pont 1090

Textures: XPT-7 Microscope with polariscope Made in Jiangnan Optical In-

strument Factcry (with the attachment of a heating plate)

Reagents: All reagents used were chemical purity and analytical reagents.

The Synthesis of Intermediates and Products.

1. Compounds 8～11 were synthesized according to ref [5,6]

2. Compounds 1,2,5,6 were synthesized as follows.

4. 5mol 8 and 50 mL anhydrous dioxane were put in 100 mL three-necked flask equipped with a condenser, $CaCl_2$ drying tube and magnetic strirrer. Seperatly, 3. 5mmol 6-1 (4-hydroxy-benzo-15-crown-5), 3. 5mmol 6-2 (4-amino-benzo-15-crown-5), 2. 0mmol cis-4,4′-diamino-dibenzo-18-crown-6, 2. 0 mmol trans-4,4′-diamino-dibenzo-18-crown-6 in 20mL anhydrous dioxane and 2mL pyridine was added dropwisedly. The mixture was stirred for 25hrs at 70℃ in a nitrogen enviroment. Solvent was evaporated and the residue was washed 3 times with water. Crude product was recrystallized from DMF for 2 times.

Compound 1 was yellowish powder, Yield 50%, Elementary Analysis. Cald. ($C_{41}H_{46}O_{10}$) C: 70. 4%, H: 6. 63%; Found: C: 70. 60%, H: 6. 39%. IR(ν_{max}/cm^{-1}, 1738, 1603, 1498, 1273, 1198, 1162, 1069. M/Z 698(M^+, 24%)

Compound 2 was white powder crystal. Yield 50%. Elementary Analysis, Cald. ($C_{41}H_{47}O_9N$) C: 70. 57%, H: 6. 79%, N: 2. 01%, Found: C: 71. 02%, H: 6. 83%, N: 2. 18%, IR(ν_{max}/cm^{-1}): 3322, 1738, 1642, 1603, 1511, 1258, 1059. M/Z: 695($M-2^+$)

Compound 5was plain yellowish powder Yield 50%. Elementary Analysis, Cald. ($C_{47}H_{78}O_{14}N_2$)C: 72. 89%, H: 6. 44%, N: 2. 30%. Found C: 72. 58%, H: 6. 23%, N: 2. 15%. IR(ν_{max}/cm^{-1})3388, 1738, 1691, 1604, 1514, 1254, 1066, 1161, 1200 ^{1}HNMR, δ_H(DMSO): 8. 30－7. 25(30H, m), 3. 97－3. 21(20H, m), 1. 43－1. 15(20H, m), 0. 89(6H, t) ppm

Compound 6was plain yellowish powder. Yield 50%. Elementary Analysis, Cald. ($C_{74}H_{78}O_{14}N_2$)C: 72. 89%, H: 6. 44%, N: 2. 30%, Found. C: 72. 60%, H: 6. 27%, N: 2. 13%. IR(ν_{max}/cm^{-1})3388, 1738, 1691, 1601, 1509. 1269, 1066, 1160, 1200

3. 4-(4′-heptoxyl-1, 1′-biphenyl-4-carboxyloxyl benzylideneamino) benzo-15-crown-5 (3)

Into 100mL three-necked flask equipped with a condenser and magnetic stirrer. 1. 10g (3. 88mmol) 4-amino-benzo-15-crown-5, 1. 45g (3. 48 mmol) 4-(4′-heptoxyl-1, 1′-biphenyl-4-carboxyloxyl) benzoyl aldehyde and 50mL alcohol were added. Refluxed in the atmosphere of nitrogen for 5. 5hours. cooled and filtered. crude product was recrystallized from chloromethene. 0. 98g grey powder was ob-

tained. Yield 41%. Elementary Analysis, Cald. ($C_{41}H_{47}O_8N$) C: 72.25%, H: 6.90%, N: 2.06%. Found. C: 71.86%, H: 6.78%, N: 2.21%. IR (ν_{max}/cm^{-1}) 1736, 1654, 1603, 1497, 1273, 1084. M/Z: 681(M^+)

4. 4-(4′-heptoxyl-1, 1′-biphenyl-4-carboxyloxyl-phenylazo) benzo-15-crown-5 (4)

Into 100mL three-necked flask, equipped with condenser $CaCl_2$ drying tube 1.25g (3.2 mmol) 4-(4′-hydroxyl phenylazo) benzo-15-crown-5 (9), 30mL anhydrous pyridine and 1.05g (3.20mmol) (11) were added. Refluxed in the atmosphere of nitrogen for 5 hours at 75 C. Cooled and poured the liquid into cold water to yield precipitate. Filtered, washed with water to obtain crude product. Ran column chromography (silica gel G), using chloroform and acetone (v/v 5 : 1) as eluent to get pure product 1.5g Yield 68%.

Elementary Analysis, Cald. ($C_{40}H_{46}O_8N_2$) C: 70.38%, H: 6.74%, N: 4.11%. Found. C: 70.01%, H: 6.85%, N: 4.02%. IR (ν_{max}/cm^{-1}) 1725, 1575, 1601, 1490, 1250, 1050, 1175, 1120. M/Z: 682(M^+) ^{1}HNMR, δ_H($CDCl_3$): 8.3−6.8(15H, m), 4.2−3.5 (18H, s), 1.8−1.2(10H, m), 0.9−0.7(3H, t)

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