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Synthesis of diaza-crown-ether cholesteric liquid crystals

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Five diaza-crown-ethers were synthesized and four of them shown to have smectic liquid crystalline properties. Their properties were determined by DSC and polarized microscopy. This type of smectogenic diazacrown ether has not been reported so far. A novel lyotropic crown ether liquid crystal was obtained from the thermotropic crown ether liquid crystal 7.

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1. Introduction

Since the idea of electroconducting mesomorphic crown ethers was for the first time put forward by Bogatskaya *et al.* [1], in 1982, nematic [2], tubular [3], polymer [4] liquid crystal crown ethers have been reported. In this work we have attempted to synthesize some diaza-crown-ethers which exhibit smectic liquid crystallinity. The scheme of the reaction was as on the next page:

2. Results and discussion

Compound **3** was prepared by a nucleophilic acyl substitution reaction between compounds **1** and **2**, using 0·5 ml pyridine as the catalyst. Compound **4** was prepared by the same reaction between compound **2** and Krytofix-22. The use of different solvents was dictated by the solubility of the diazo-crown-ether.

Compounds **6** and **7** were prepared by complete or partial substitution of Kryptodix-22.

Unfortunately, the reaction of krytofix-22 and cholesteryl halopronionate as starting materials results in mixtures that do not contain compound **9**. However, the preparation of compound **9** was readily achieved under nitrogen in the presence of *p*-toluenesulphonic acid, reacting compound **8** with cholesterol in anhydrous benzene.

Crown ethers **4**, **6**, **7** and **9** exhibited smectic LC phases by DSC and polarizing microscopy. The results are given in the table and figures 1–4. Comound **3** did not possess liquid crystallinity owing to the 12-crown-4 ether ring structural unit having no planarity.

We have also found that when compound **7** was mixed with dilute hydrochloric acid or with dilute hydrochloric acid and isopropyl myristate the thermotopic liquid crystal **7** became lyotropic. The textures of the lyotropic crown ether liquid crystal **7** are given in figures 5 and 6.

3. Experimental

3.1. *Instruments*

Infrared spectra were recorded on a Nicolet FT-IR 170SX spectrophotometer. ^{1}H NMR spectra were recorded on a JNM-FX90Q spectrometer in $CDCl_3$. Mass spectra were obtained on a Hitachi M-80 AGS-MS system. Combustion analyses for C and H were performed on a Carlo Erba 1106 element analysis instrument. DSC were recorded on a Dupont 1090 thermal analysis instrument.

3.2. *Synthesis of intermediates and products*

Intermediates **1**, **2**, **5** and **8** were synthesized by the methods given in references [5], [6], [7] and [8], respectively.

Compound **3**: Compound **1** (0·40 g, 2·30 mmol) was dissolved in anhydrous benzene (10 ml). Under a N_2 atmosphere, a solution of compound **2** (2 g, 4·64 mmol) in dry benzene (10 ml) and anhydrous pyridine (0·5 ml) were added dropwise over 1 h at 40°C. After the addition was complete, the mixture was refluxed for an additional 12 h at 40°C. The mixture was filtered, the filtrate distilled at a reduced pressure to remove the solvent and the crude product **3** was obtained. The product was purified by chromatography on a silica gel column (AcOEt–light petroleum, 1:5, V/V, R_f 0·30), and then recrystallized from anhydrous dioxane to give white powder (1·21 g). Yield, 52·0 per cent; m.p. 260–261°C, IR (KBr): 1696 (C=O), 1128 (C–O–C) cm^{-1}: ^{1}H NMR ($CDCl_3$): 5·35 (2 H, s, 2 × C=CH), 4·50 (2 H, s, 2 × OCH), 3·69 (8 H, s, 4 × CH_2N), 3·45 (8 H, s,

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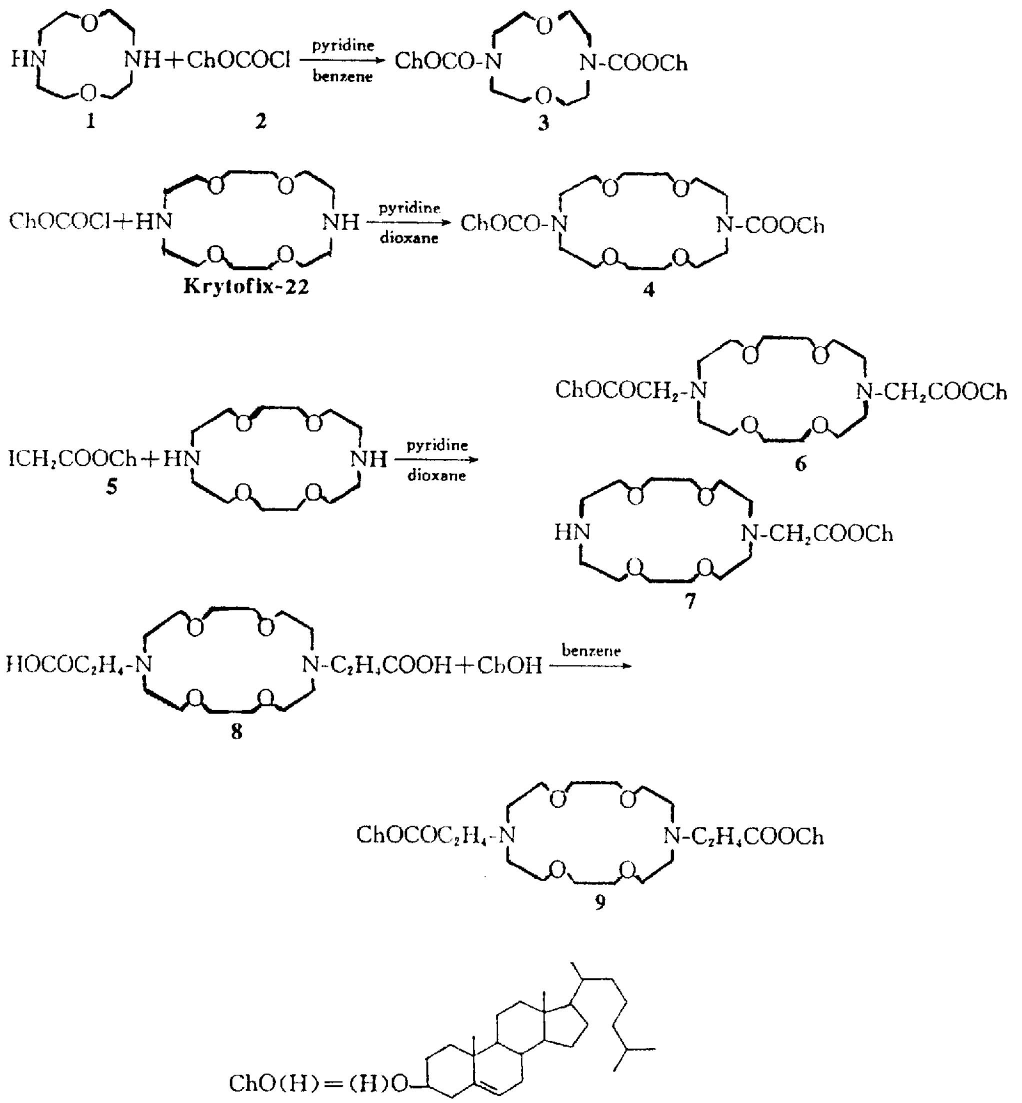

Table. The transition temperature and enthalpy change of crown ethers.

Compounds	Phase transition temperature/°C (ΔH/J mol^{-1})
3	Cr260I
4	Cr149·1 (4·14 × 10^4)(S) 214·6 (1·14 × 10^4)I
6	Cr125·3 (2·06 × 10^4)(S) 257·5 (3·92 × 10^4)I
7	Cr94·5 (8·26 × 10^4)(S) 210·6 (2·68 × 10^3)I
9	Cr173·2 (7·32 × 10^3)(S) 203·5 (3·77 × 10^4)I

Cr crystal; S, smectic; I, isotropic.

4 × CH_2O), 2·55–0·67 (86 H, m, cholesteryl ring). *m*/*z* 998 $[M]^+$. Found: C, 76·93; H, 10·88; N, 2·85 per cent. Calculated for $C_{64}H_{106}O_6N_2$: C, 76·95; H, 10·62; N, 2·80 per cent.

Compound **4**: Compound **2** (2·9 g, 6·46 mmol), anhydrous pyridine (0·5 ml), and kryptofix-22 (0·78 g, 2·98 mmol) were dissolved in anhydrous dioxane (70 ml). Under a N_2 atmosphere the mixture was stirred at reflux for 13 h, then filtered. The filtrate was distilled at a reduced pressure to remove the solvent and the crude product **4** obtained. This was recrystallized from anhydrous dioxane to give white crystals (1·75 g). Yield, 51·0 per cent, T_{CrS} 149·1°C, T_{SI} 214·6°C. IR (KBr): 1689 (C–O), 1140 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$): 5·36 (2 H, s, 2 × C=CH), 4·15 (2 H, s, 2 × OCH), 3·65 (8 H, s, 4 × CH_2N), 3·40 (16 H, s, 8 × CH_2O), 2·67–0·63 (86 H, m, cholesteryl ring) ppm. *m*/*z* 1087 $[M+1]^+$. Found: C, 75·26; H, 11·15; N, 2·62 per cent. Calculated for $C_{68}H_{114}N_2$: C, 75·14; H, 10·80; N, 2·58 per cent.

Compounds **6** and **7**: Compound **5** (1·69 g, 3·05 mmol), kryptofix-22 (0·40 g, 1·53 mmol), anhydrous pyridine (0·5 ml), and anhydrous dioxane (50 ml) were mixed under nitrogen. The mixture was stirred at reflux for

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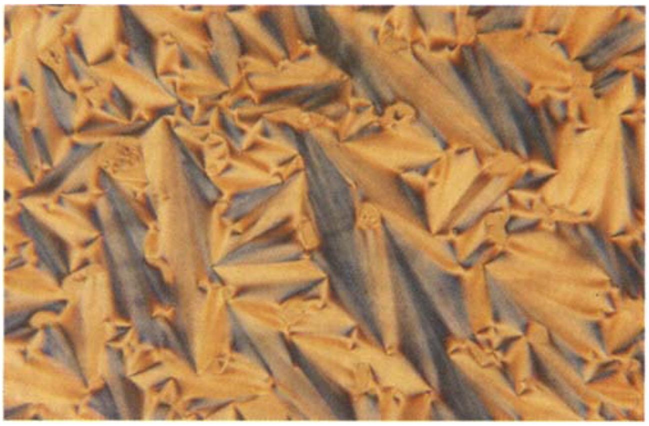

Figure 1. Texture of compound **4** (175°C, on cooling) × 150.

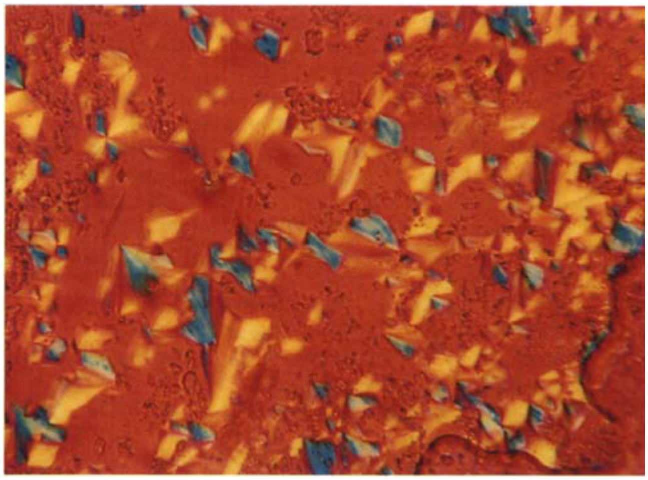

Figure 2. Texture of compound **6** (162°C, on heating) × 130.

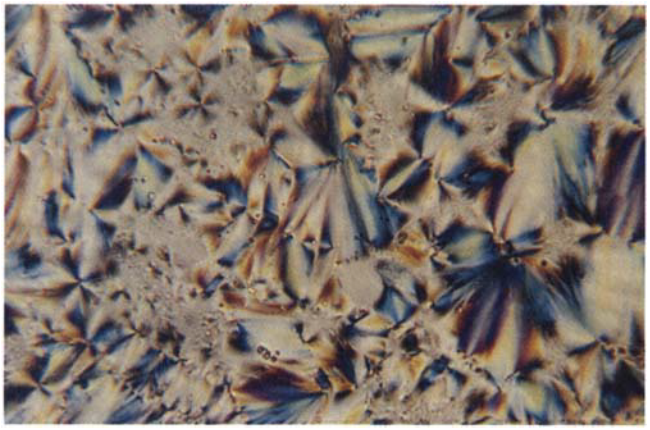

Figure 3. Texture of compound **7** (135°C, on heating) × 150.

78 h, then filtered. The solvent was evaporated and the residue was chromatographed using 33 per cent chloroform in acetone to give **6** (0·47 g, R_f 0·55) and **7** (0·12 g, R_f 0·35).

Compound **6**: T_{CrS} 125·3°C, T_{SI} 257·5°C. IR (KBr):

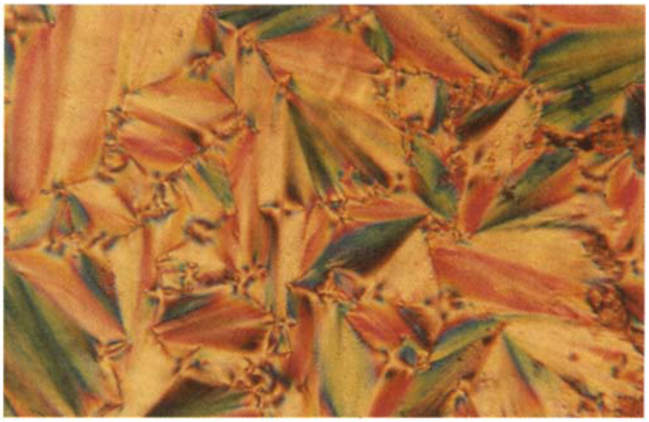

Figure 4. Texture of compound **9** (191°C, on cooling) × 150.

Figure 5. Texture of compound **7** mixed with dilute hydrochloric acid at 20°C.

Figure 6. Texture of compound **7** mixed with dilute hydrochloric acid and isopropyl myristate.

1725 (C=O), 1121 (C–O–C) cm^{-1}; ^{1}H NMR ($CDCl_3$): 5·58 (2 H, s, 2 × C=CH), 4·86 (2 H, s, 2 × OCH), 3·81 (8 H, s, 4 × CH_2N), 3·60 (16 H, s, 8 × CH_2O), 2·99 (4 H, s, 2 × NCH_2=O), 2·70–0·73 (86 H, m, cholesteryl ring) ppm. *m/z* 1116 [m + 2]$^+$. Found: C, 73·38, H, 10·63; N, 2·55 per cent. Calculated for $C_{70}H_{118}O_8N_2$: C, 73·40, H, 10·59; N, 2·57 per cent.

Compound **7**: $[\alpha]_D^{10} = -15{\cdot}93$ (c, 0·251, $CHCl_3$) T_{CrS} 94·5°C; T_{SI} 210·6°C. IR (KBr): 3340 (N–H), 1734 (C=O), 1130 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$): 5·33 (1 H, s, C–CH), 4·58 (1H, s, OCH), 3·99 (4 H, s, 2 × CH_2N), 3·60 (4 H, s, 2 × CH_2N), 3·10 (16 H, s, 8 × CH_2O), 2·40–0·51 (44 H, m, NH and cholesteryl ring). *m/z* 689 [m + 1]$^+$. Found: C, 71·68; H, 10·22; N, 3·88 per cent. Calculated for $C_{41}H_{72}O_6N_2$: C, 71·51; H, 10·46; N, 4·07 per cent.

Compound **9**: Compound **8** (1·00 g, 2·46 mmol) and cholesterol (1·90 g, 4·92 mmol) were heated at reflux with azeotropic dehydration for 14 h in 50 ml of benzene containing 0·05 g of *p*-toluenesulphonic acid as the catalyst under nitrogen. The solvent was then evaporated *in vacuo* and the residue was separated by VLC [9] on silica gel using chloroform and acetone as stepwise eluants. White crystals **9** were obtained in a yield of 45 per cent, T_{CrS} 173·9°C, T_{SI} 203·5°C. IR (KBr): 1730 (C=O), 1100 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$): 5·29 (2 H, s, 2 × C=CH), 4·55 (2 H, s, 2 × CH), 3·80 (8 H, s, 4 × CH_2N), 3·45 (16 H, s, 8 × CH_2O), 2·81 (8 H, s, 2 × C=CH), 2·70–0·63 (86 H, m, cholesteryl ring) ppm. *m/z* 1143 [m + 1]$^+$. Found: C, 75·75; H, 10·60; N, 2·14 per cent. Calculated for $C_{72}H_{122}O_8N_2$: C, 75·66; H, 10·68; N, 2·46 per cent.

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References

[1] Bogatskaya, L. C., Lukyanenko, N. G., Kulygine, E. Yu., and Nesternko, N. L., 1982, Ninth International Conference on Liquid Crystals, Programmed and Abstracts, Bangalore, p. 15.

[2] (*a*) Xie, M. G., Hunag, S., and Wang, L. Y., 1984, Third National Conference on Crownether Chemistry of China, Vol. 1, Tai Chang, China; (*b*) Lilatob, Yu. S., Tsukruk, V. V., Shchilov, V. V., Lastushchok, V. N., Galatina, A. I., and Vogatskii, A. V., 1985, *Dokl. Adad. Nauk. (Fieh. Khim), CCCP*, **285,** 155; (*c*) Shinkai, S., 1987, *Jpn. Kokai Tokkyo Koho*, **87,** 74; (*d*) Xie, M. G., Qin, J., Hong, F., and Wang, L. Y., 1991, *Acta chem. Sinica*, **49,** 297; (*e*) He, G. X., and Matsuda, T., 1987, *J. chem. Soc. chem. Commun.*, 1287.,

[3] Lehn, J. M., Malthete, J., and Levelut, A. M., 1985, *J. chem. Soc. chem. Soc. chem. Commun.*, 1974.

[4] (*a*) Percec, V., and Rodenhouse, R., 1988, *Polym. Prepr.*, **29,** 296; 1990, *ibid.*, 81; (*b*) Ehnev, V. V., Romanova, M. S., Skorokhodov, S. S., and Koton, M. M., 1988, *V'ylsokomokek. Soed. V,* **30,** 610; (*c*) Cowie, J. M. G., and Wu, H. H., 1988, *Br. Polym. J.*, **20,** 515; (*d*) Perec, V., and Rodenhouse, R., 1989, *Macromolecules*, **22,** 2043.

[5] Lehn, J. M., 1976, US Patent 3 966 766.

[6] Bergstern, C. G., 1959, US Patent 2 889 318.

[7] Barton, D. H. R., Pradhan, S. K., Sternhell, S., and Templeton, J. F., 1961, *J. chem. Soc.*, 225.

[8] Takagi, M., Tazaki, M., and Ueno, K., 1978, *Chem. Lett.*, 1179.

[9] Zheng, G. C., 1989, *YouJi HuaXue*, **9,** 286.

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