Nematic Liquid Crystal Compounds containing a Benzocrown Ether Unit

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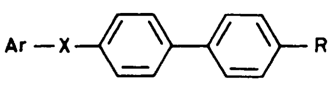
Benzocrown ethers carrying a *para*-substituted biphenyl group, (**1a**—**c** and **2a,b**), display a nematic liquid crystal phase; selective complexation with picrates in the liquid crystal phase was observed by doping experiments.

Numerous crown ether compounds have been synthesized since the pioneering work of Pedersen 20 years ago.[1] In addition to the study of the relationship between the structure of crown ethers and their complexing ability, many efforts have been made to utilize crown ethers as selective ionophore units in other functional compounds, *e.g.*, amphiphiles bearing a crown ether unit as a hydrophilic head group[2] and bilayer membranes which show a selective effect on addition of metal cations in aqueous solutions.[3] Lehn *et al.* reported that the hexa-(*p*-n-dodecyloxybenzoyl) derivatives of the macrocyclic polyamines show a tubular mesophase.[4]

There has been much interest in new liquid crystal materials

Table 1. Transition temperatures (°C) of compounds with structure:



Compound	Ar[b]	X	R	K–N[a]	N–I[a]	K–I[c]
(**1a**)	B15C5	$-CO_2-$	CN	184	186	—
(**1b**)	B18C6	$-CO_2-$	CN	183	(154)	—
(**1c**)	B15C5	$-CO_2-$	OC_8H_{17}-n	157	(148)	—
(**1d**)	B15C5	$-CO_2-$	C_7H_{15}-n	—	—	158
(**2a**)	B15C5	$-C{\equiv}C-$	CN	218	(202)	—
(**2b**)	B18C6	$-C{\equiv}C-$	CN	181	(165)	—
(**2c**)	B15C5	$-C{\equiv}C-$	C_7H_{15}-n	—	—	168
(**3a**)	B15C5	$-CH_2CH_2-$	CN	—	—	144

[a] K, N, and I represent crystal, nematic, and isotropic phases, respectively. Parentheses indicate monotropic transitions. [b] B15C5 and B18C6 = 4′-substituted benzo-15-crown-5 and benzo-18-crown-6, respectively. [c] (**1d**), (**2c**), and (**3a**) do not show any mesophases.

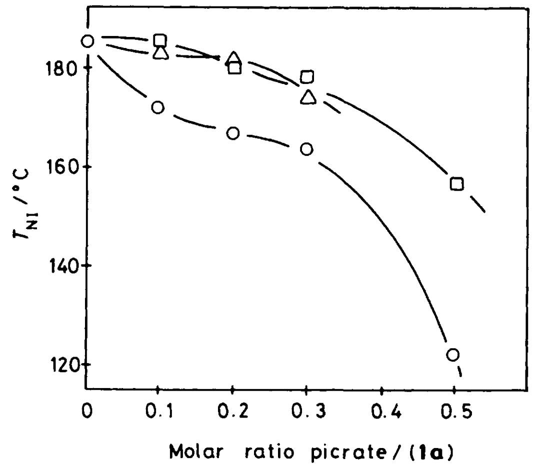


Figure 1. Effect of picrate doping (○, sodium; □, potassium; △, tetramethylammonium) on nematic–isotropic transition temperature (T_{NI}) of (**1a**).

because of their physico-chemical properties and potential applications. Of particular interest is the possibility of combining the complexing properties of crown ethers with the supramolecular arrangements provided by the mesophases of liquid crystal compounds. We now show that it is possible to form a nematic mesophase by a new liquid crystal compound containing a benzocrown unit, and also report preliminary investigations of the effects of the presence of the crown unit and the complexation with cations on the supramolecular properties.

Compounds (**1a**—**d**) were obtained by treating 4′-chlorocarbonyl benzocrown ethers with *p*-hydroxybiphenyl derivatives in the presence of pyridine (2 equiv.) in benzene. 4′-Ethynylbenzocrown ethers were treated with *p*-iodobiphenyl derivatives to give (**2a,b**).[5] The products were purified by recrystallization from acetone and their structures were confirmed by ^{1}H n.m.r. and i.r. spectroscopy and elemental analyses. Their thermal and optical properties were studied using a differential scanning calorimeter and a micro melting point apparatus equipped with a polarizer. The transition temperatures are given in Table 1.

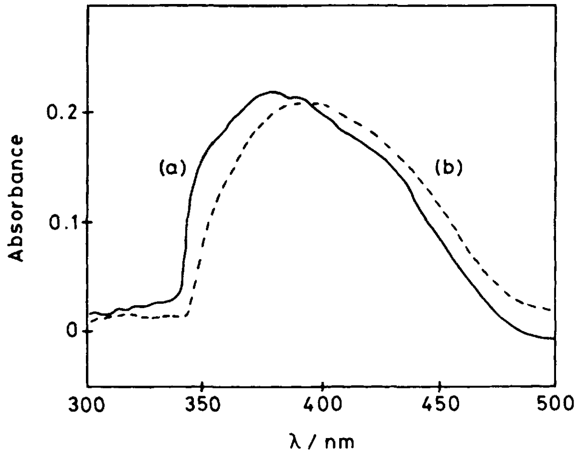


Figure 2. U.v. spectra of sodium picrate in (**1a**): (a), isotropic liquid phase; (b), nematic liquid phase. Molar ratio sodium picrate : (**1a**) = 5 : 1000.

The benzocrown ether derivatives (**1a**—**c**) and (**2a,b**) display a nematic liquid crystal phase (schlieren or marbled texture). As shown in Table 1, replacement of the B15C5 with the B18C6 unit depresses the nematic–isotropic transition temperature (T_{NI}), probably because the B18C6 unit is more flexible and larger than the B15C5 unit. A nematic phase is not observed if the biphenyl moiety contains a heptyl substituent. The liquid crystal behaviour is observed for compounds with both ester and acetylene linking groups, but not for compound (**3a**) with a dimethylene linking group.

Figure 1 shows the effect of picrate doping on T_{NI} of (**1a**).† Potassium and tetramethylammonium picrate, which cannot be complexed by the crown unit, show a similar effect, whereas T_{NI} values were decreased markedly on doping with sodium picrate, probably owing to the selective complexation of the benzo-15-crown-5 unit with sodium picrate. The selective binding in the liquid crystal phase of (**1a**) is also shown by u.v. spectroscopy (Figure 2).‡ Doping of (**1a**) with sodium picrate led to a red shift ($\lambda_{max.}$ changes from 380 to 390 nm) when (**1a**) changes from isotropic liquid phase to nematic liquid crystal phase, but potassium picrate ($\lambda_{max.}$ 385 nm) and tetramethylammonium picrate ($\lambda_{max.}$ 385 nm) did not show such shifts. A similar shift was observed on doping (**1b**) with potassium picrate, but not with sodium and tetramethylammonium picrates. A red shift of picrates in solution is often associated with the formation of separated ion pairs in complexation with crown ethers.[6] Thus the red shift observed here can be explained by the formation of a more widely separated ion pair between the complexed cation and picrate

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† The samples were prepared by dissolving the picrates in dichloromethane solutions of the crown ether compounds. After removal of solvent under reduced pressure at room temperature, pale yellow solids were obtained which were melted completely once before the measurements.

‡ U.v. spectra were measured by a multi-channel spectrophotometer (MCPD-100, Otsuka Electronics) equipped with a hot plate. Thickness of samples: 50—80 nm.

anion restricted by the liquid crystal molecules in the nematic phase.

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