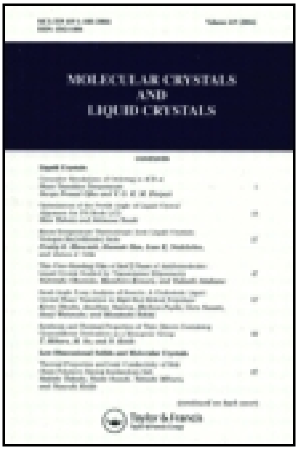

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Liquid Crystal Donor-Acceptor Complexes

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LIQUID CRYSTAL DONOR-ACCEPTOR COMPLEXES

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Abstract A number of binary mixtures of potentially mesogenic compounds can produce liquid crystals if donor-acceptor complexes are formed by the component molecules.

INTRODUCTION

The vast literature on donor-acceptor complexes consists predominantly of studies made in solution and in the solid state, and, to some extent, in the vapor phase. Recently, the number and variety of compounds that form liquid crystals have grown steadily and the binary mixtures have been extensively examined because of wide industrial utility and of reliability as the method of identification. Nevertheless, studies on the donor-acceptor complexes in the liquid crystalline state, often called the fourth state of matter, are rather scanty. This paper mostly deals with liquid crystal complexes formed by mixing of potentially mesogenic donor and acceptor compounds. In other words, component compounds are nonmesogenic but the molecules of which are elongated and lath-like in shape.

EXPERIMENTAL

The structral formulas of the component compounds studied so far are shown on next page. The calorimetric curves were recorded on a Rigaku differential scanning calorimeter during the processes of heating and cooling. The liquid crystals were identified by examining their texture with the aid of a polarizing microscope an/or by studying the continuous miscibility with a reference mesogen.

RESULTS AND DISCUSSION

The liquid crystal complexes appearing in the binary mixtures consisting of the 4-dimethylamino-4-alkoxy and 4-nitro-4-alkoxy derivatives of N-benzylideneaniline are summarized in Table 1[1]. The component compounds represented by their terminal substituents in parentheses are accompanied by the latent nematic-isotropic (N-I) transition temperature in °C. They were deduced by the extrapolation of N-I transition point curves observed in the binary systems with nematogenic azoxydianisole. Here, N and S stand for nematic and smectic A phases respectively. Phases in parentheses are monotropic. The symbol N is followed by the extent of stabilization of a mesomorphic complex defined by the deviation of the transition point curve at 50 mol% from a straight line joining the latent transition temperatures of the donor and acceptor compounds. The following tendencies may be noted; first, the extent of stabilization of an N complex increases with an

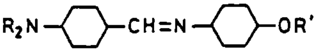
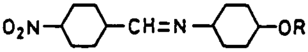
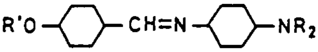
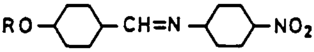
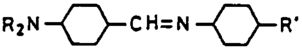
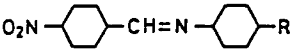
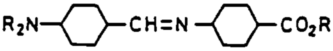
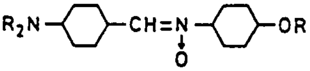
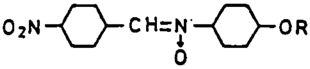
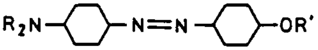
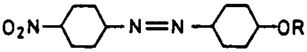
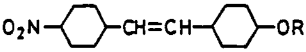
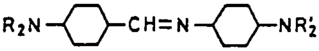
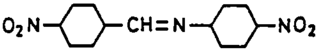
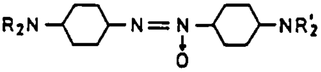
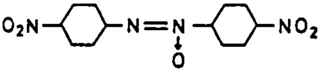
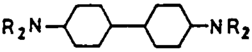
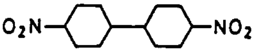
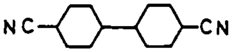
DONOR	ACCEPTOR
	
(R_2N, $R'O$)	(O_2N, RO)
	
($R'O$, NR_2)	(RO, NO_2)
	
	
	
⟨R_2N, $R O$⟩	⟨O_2N, RO⟩
	
	
	
	
	
	

TABLE 1. Liquid crystals induced in the donor-acceptor systems and the extent of stabilization of the nematic complex at the mole ratio of 1:1 in °C.

	Donor					
Acceptor	(Me_2N,MeO) 55	(MeO,Me_2N) 60	(Me_2N,EtO) 97.5	(EtO,Me_2N) 102	(Me_2N,PrO) 75	(PrO,Me_2N) 75
(NO_2,MeO) 80			(N) 20	(N) 19	(N) 27 (S)	N 30 (S)
(MeO,NO_2) 82	(N) 30	(N) --	N 11	N 7	N 22 (S)	N 17 (S)
(NO_2,EtO) 85	(N) 38	(N) 37	(N) 32	N 31	(N) -- (S)	(N) 40 (S)
(EtO,NO_2) 90	N 33	N 30	N 27	N 23	N 26 (S)	N 26 (S)
(NO_2,PrO) 50	(N) 49 (S)	(N) 49 (S)	(S)	(N) 42 (S)		(N) -- (S)
(PrO,NO_2) 57.5	N 43 (S)	N 37 (S)	(N) 33 (S)	N 30 (S)	(N) -- (S)	(N) -- (S)

increase of the alkoxyl chain length when a given donor is combined with acceptors of the particular type, say (RO,NO_2). Second, when the acceptor molecule carries a longer alkoxyl group than the donor molecule does, the stability of an N complex is higher compared with that of the complex in which the alkoxyl groups are interchanged. Third, the extent of stabilization of an N complex of the acceptor of the type (NO_2,RO) is larger than that of the acceptor of the type (RO, NO_2).

The solid complexes formed with acceptors of the type (NO_2,RO) are thermally more stable than those formed with acceptors of the type (RO,NO_2). In addition, the combinations of the donor and acceptor molecules with the same alkoxyl groups lead to solid complexes more stable than those given by the molecules with different alkoxyl groups. As the maximum temperature of the N-I transition point curve is not very sensitive to the interchange in the positions of terminal substituents, especially those in donor molecules, the stable existence of an N complex is largely associated with the absence of a solid complex or the formation of an incongruently melting complex as exemplified by the phase diagrams for the (Me_2N,EtO)-(NO_2,EtO) and (Me_2N,EtO)-(EtO,NO_2) systems presented in Figure 1[2,3].

The thermal stability of S complex is markedly affected by the positions of the substituents. If the two mesomorphic complexes arise by mixing, the separation between the N-I and S-N

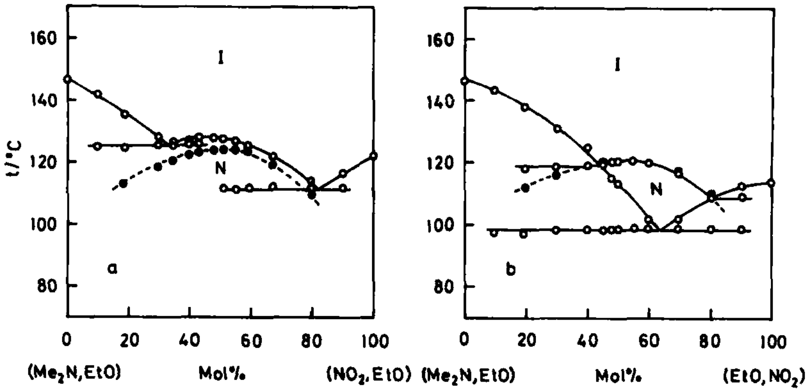


FIGURE 1. Phase diagrams of (a) (Me_2N,EtO)-(NO_2,EtO) and (b) (Me_2N,EtO)-(EtO,NO_2) systems. The open and shaded circles are transitions recorded in the processes of heating and cooling respectively.

transition point curves increases in this order; (RO,Me_2N)-(NO_2,R'O) $<$ (Me_2N,RO)-(NO_2,R'O) $<$ (RO,Me_2N)-(R'O,NO_2) $<$ (Me_2N,RO)-(R'O,NO_2) regardless of the kind of alkoxyl groups. In some cases, an S complex is so much stabilized that supercooled liquid is directly transformed into a metastable S complex in a certain composition range.

In order to clarify the relations between the stability of liquid crystal complexes and molecular structure, studies on the effects of substituents and central linkages are obviously important. Figure 2 presents examples of the former studies. The replacement of the Me_2N group in the (Me_2N,EtO)-(NO_2,EtO) system by an Et_2N group results in the formation of an S complex instead of

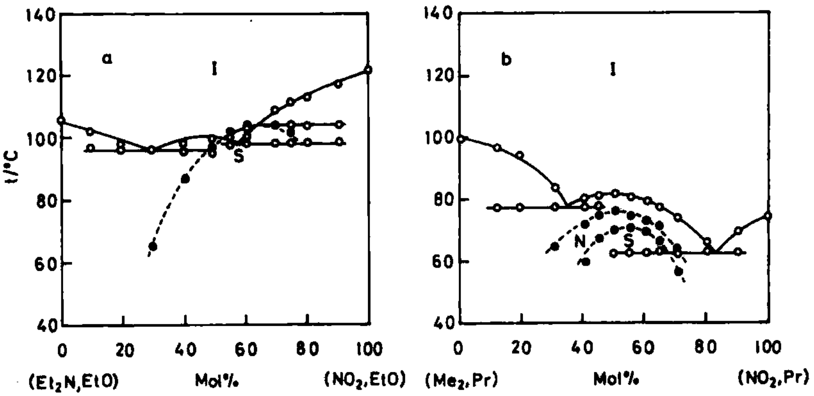


FIGURE 2. Phase diagrams of (a) (Et_2N,EtO)-(NO_2,EtO) and (b) (Me_2N,Pr)-(NO_2,Pr) systems.

an N complex[4]. The maximum of the S-I transition point curve is located around 60 mol% of the acceptor. The thermal stability of the solid complex is diminished by this replacement. Another example in Figure 2 indicates the effect of the replacement of the alkoxyl groups in (Me_2N,EtO) and (NO_2,EtO) by propyl groups[3]. Not only an N complex but also an S complex are formed in this system.

The effect of central double bond linkage on liquid crystal formation is demonstrated employing -N=N- and -CH=NO- groups. No solid complex is found in the phase diagram of the 4-dimethylamino-4'-ethoxyazobenzene (DMAEA)-4-ethoxy-4'-nitroazobenzene (ENA) system, as is shown in Figure 3[5]. An N phase appearing as a single phase in a rather narrow composition range is stabilized as much as 18 °C by complex formation. The diagram

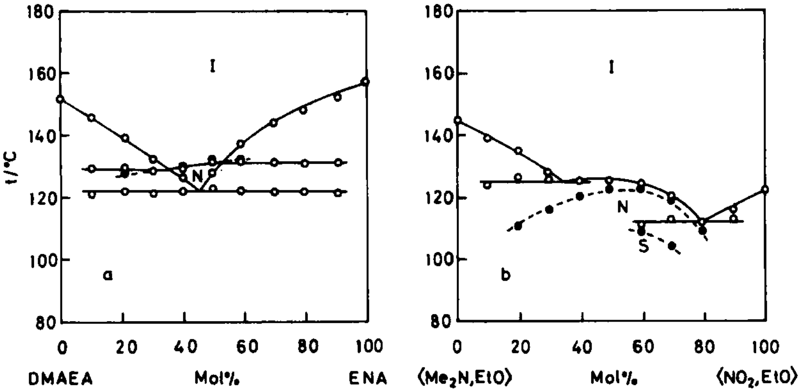


FIGURE 3. Phase diagrams of (a) DMAEA-ENA and (b) $\langle \mathrm{Me_2N,EtO} \rangle$-$\langle \mathrm{NO_2,EtO} \rangle$ systems.

produced by the nitrones $\langle \mathrm{Me_2N,EtO} \rangle$ and $\langle \mathrm{NO_2,EtO} \rangle$ is very much alike to that by ($\mathrm{Me_2N}$,EtO) and ($\mathrm{NO_2}$, EtO)[6]. However, there is one significant difference between the two systems; that is, a metastable S complex is formed with the nitrones (Compare Figures 1a and 3b).

Binary mixtures comprising ($\mathrm{NO_2,NO_2}$) and ($\mathrm{Me_2N}$,RO) or (RO,$\mathrm{Me_2N}$) produce N and S complexes when RO = EtO, but only an S complex when RO = PrO[7]. The liquid crystal complexes appear in the range centered around 30 mol% of ($\mathrm{NO_2,NO_2}$). Similarly, liquid crystal complexes are formed in several mixtures of ($\mathrm{R_2N,R'_2N}$) with ($\mathrm{NO_2}$,RO) or (RO,$\mathrm{NO_2}$). The bis(dialkylamino) and dinitro derivatives of azoxybenzene, N,N,N',N'-tetramethylbenzidine (TMB), 4,4'-dinitrobiphenyl (DNBP), and 4,4'-dicyanobiphenyl (DCNBP) were shown to be efficient as one of the component compounds in producing liquid crystal complexes[8].

The effects of branching of ester alkyl group on the formation of mesomorphic donor-acceptor complexes were studied employing the alkyl 4-[4-(dimethylamino)benzylideneamino]benzoate-4,4'-dinitroazoxybenzene (DNAO) systems[9]. S complexes are formed not only in the systems with normal alkyl esters but also with esters of branched alkyl groups such as t-butyl, 1,2-dimethylpropyl, and 1-ethylpropyl. The maximum temperatures of the S-I transition point curves are almost idencal for the complexes with the isopropyl and t-butyl esters. Moreover, the liquid crystal complex formed with the 1-methylpropyl ester is more thermally stable than that formed with the 2-methylpropyl ester. The stability of the 1,2-dimethylpropyl ester complex is intermediate between those of the afore-mentioned two. These results are outstandingly different from those reported for single mesogenic compounds.

Finally, it may be interesting to add that S liquid crystal complexes can be produced by the addition of the following benzene derivatives to nematogenic N-(4-propoxybenzylidene)-4-hexylaniline; 4-alkoxynitrobenzenes, 4-nitrophenyl alkanoates, alkyl 4-nitrobenzoates, N-(4-nitrophenyl)-alkanamides, and their cyano analogs[10,11]. 4-Nitrophenyl alkanoates are more efficient than alkyl 4-nitrobenzoates in stabilizing the S liquid crystal complexes. No S complex emerges in N-alkyl-4-nitrobenzamide-the Schiff's base mixtures. The phase diagrams revealed that the benzene derivatives with a CONHR or NHCOR group have their latent smectic phases near room temperature.

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