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Mesomorphic Properties of 2-(4-*n*-Alkoxybenzylideneamino)anthracenes

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Synopsis. 2-(4-*n*-Alkoxybenzylideneamino)anthracenes were synthesized, and the phase transitions were determined using a differential scanning calorimeter and a polarizing microscope. Methoxy through propoxy derivatives exhibit the monotropic nematic state, whereas the higher members show the enantiotropic nematic state.

It is well recognized that the molecules which can form liquid crystalline phases generally possess common structural features. The four structural features that appear essential are; (1) the molecules will be rod-like in shape; (2) they must be rigid; (3) the simultaneous presence of permanent dipoles and easily polarizable groups within a molecule plays an important role, and (4) weak dipoles at the end groups of the molecule are of importance.[1–4] Indeed, the molecules of an unelongated and plate-like shape exhibit no mesomorphic properties. It has, however, been found that naphthalene,[5] fluorene,[6] and phenanthrene,[7] the molecular structures of which are not rod-like, can exhibit liquid crystalline states if one introduces appropriate substituents to them. In order to elucidate the relationship between the molecular structure and the mesomorphic properties, it is of much interest that a liquid crystalline compound can be obtained by introducing the end substituent to the compounds which exhibit potentially non-mesomorphic behavior. In this paper we wish to report first that anthracene, whose molecule is plate-like and is much wider than that of naphthalene or phenanthrene, can indeed exhibit a liquid crystal state if a 4-*n*-alkoxybenzylidene group is introduced at the 2-position.

Experimental

Materials. The 2-(4-*n*-alkoxybenzylideneamino)anthracenes studied here were synthesized from 4-*n*-alkoxybenzaldehyde and 2-aminoanthracene which were themselves commercially obtained by refluxing several hours in a mixed solution of benzene and methanol. The crude products were successively recrystallized from methanol, benzene, and hexane. They were thoroughly dried under a vacuum in order to remove the solvent and any moisture.

Measurements. The transition heat was determined by means of a Rigaku differential scanning calorimeter which was calibrated in terms of the temperature and the energy using potassium nitrate, indium, benzoic acid, and tin. All the samples were packed in closed aluminium sample pans. Each sample was heated and cooled under a flow of nitrogen gas to prevent the decomposition of the sample. The phase transition and the liquid crystal texture were observed by using a polarizing microscope and a Mettler FP 52 microfurnance for sample temperature control.

Results and Discussion

All the compounds studied exhibit the nematic liquid crystal state, except for 2-(benzylideneamino)-

TABLE 1. THERMODYNAMIC DATA FOR A SERIES OF 2-(4-*n*-ALKOXYBENZYLIDENEAMINO)ANTHRACENES

		Transition		
n-Alkoxy	Transition	Temperature (°C)	Heat (cal/mol)	Entropy (cal·K^{-1}·mol^{-1})
Methoxy-	solid-isotropic	202	9550	20.1
	isotropic-nematic	199	76	0.16
Ethoxy-	solid-isotropic	199	7670	16.2
	isotropic-nematic	201	105	0.22
Propoxy-	solid-isotropic	186	8410	18.3
	isotropic-nematic	179	74	0.16
Butoxy-	solid-nematic	177	9140	20.3
	nematic-isotropic	183	91	0.20
Pentyloxy-	solid II-solid I	137	587	1.43
	solid I-nematic	165	8730	19.9
	nematic-isotropic	173	71	0.16
Hexyloxy-	solid II-solid I	124	220	0.55
	solid I-nematic	162	8990	20.7
	nematic-isotropic	174	90	0.20
Heptyloxy-	solid II-solid I	129	1600	3.98
	solid I-nematic	157	8730	20.3
	nematic-isotropic	167	79	0.18
Octyloxy-	solid III-solid II	125	910	2.29
	solid II-solid I	136	530	1.30
	solid I-nematic	154	9450	22.1
	nematic-isotropic	167	102	0.23

1 cal=4.184 J

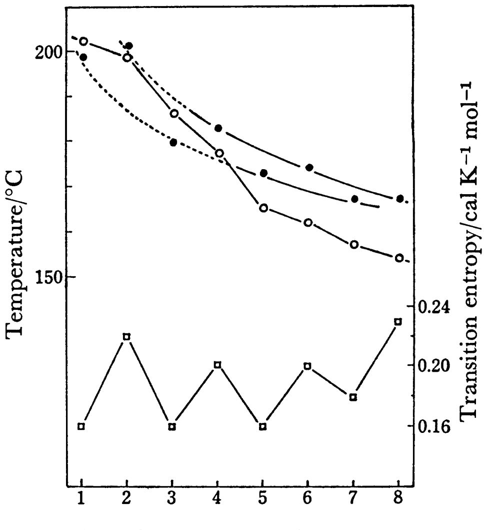

Fig. 1. Phase transition diagram and the transition entropy for 2-(4-*n*-alkoxybenzylideneamino)anthracene series.

○: Solid-nematic or isotropic; ●: nematic-isotropic; □: transition entropy for the nematic-isotropic transition. The dotted lines indicate the monotropic transitions.

anthracene, which gives no mesomorphic state. The phase-transition temperatures are summarized in Table 1, together with the calorimetric data. The first three members in this series show the monotropic nematic state, while the higher members, starting with 2-(4-*n*-butoxybenzylideneamino)anthracene, exhibit the enantiotropic nematic phase. Furthermore, the solid-solid transition is observed for the homologous series with longer alkoxy chains than pentyloxy. This is not surprising since the presence of two or more solid phases is very common with materials forming mesomorphic states.

Figure 1 shows the variation in the transition temperature with the increase in the length of the alkoxy chain. Both the solid-nematic and the nematic-isotropic liquid transition temperatures become lower as the alkoxyl group grows. In addition, an even-odd alternation of the nematic-isotropic liquid transition temperature is apparent. Such an even-odd effect for the nematic-isotropic liquid transition has frequently been found in most homologous series of liquid crystals.[1-4] In particular, for a homologous alkoxy series[1-4,8] each of the clearing points for both even and odd carbon-chain members falls on a smooth curve. In the homologous series of 2-(4-*n*-alkoxybenzylideneamino)-anthracenes studied here, two smooth curves can be drawn, as shown in Fig. 1, one connecting the even carbons and the other connecting the odd carbons. The curve for the even carbons lies above that for the odd carbons, as in other homologous alkoxy series. The even-odd alternation can be understood as a consequence of the even-odd effect in the chain-order parameter with respect to the molecular axis.[9] The entropies of transition for the nematic-isotropic liquid transition are also shown in Fig. 1. As is expected in view of the results mentioned above, the transition entropy shows the even-odd alternation more striking than the transition temperature.

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