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Liquid Crystalline Properties of 4-Octyloxybiphen-4'-yl 4-Hydroxybenzoate and 4-Hydroxyphenyl 4-Octyloxybiphenyl-4'-carboxylate

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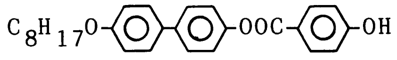
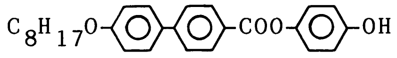
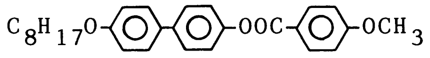
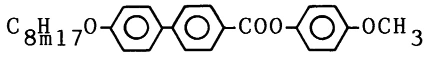
4-Octyloxybiphen-4'-yl 4-hydroxybenzoate and 4-hydroxyphenyl 4-octyloxybiphenyl-4'-carboxylate show a nematic phase, and the former compound also shows abnormally stable smectic A phase, where an associated hydrogen bond complex is assumed to be the origin.

It is well known that some liquid crystals having a nitro or a cyano group form an antiparallel dimer due to a strong dipole-dipole interaction, and show a smectic A phase having a bilayer arrangement(S_{A2}), and also a monolayer one(S_{A1}) due to the thermal dissociation of the associated dimer. In such conditions, the molecule experiences a S_{A2}-S_{A1} transition.1) It is also known that many liquid crystals having a carboxy group at the terminal position form an associated dimer due to hydrogen bond, and show an antiferroelectric-type smectic C phase when the alkyl chain is sufficiently long.2) However, the molecule does not show such diversity in the smectic C phase since the hydrogen bond is strong enough to keep the associated state within the mesomorphic temperature range. On the other hand, the development of liquid crystals having a a hydroxy group at the terminal position is quite rare,3) maybe due to the fact that the hydrogen bond remarkably enhances the melting point.

In this paper, we want to describe the effect of the hydrogen bond on the mesomorphic properties for 4-octyloxybiphen-4'-yl 4-hydroxybenzoate(1) and 4-hydroxyphenyl 4-octyloxybiphenyl-4'-carboxylate(2).

The results are summarized in Table 1, where the thermal data for the

Table 1. Transition temperatures and latent heats for compounds 1 - 4

Compound number	Structure	Transition temperatures(T/°C)[a] latent heats(kJ/mol)
1		C-211(-S_A-204-N-209)-I 50 1.8 2.8
2		C-180[-S_A-165]-N-210-I 45 - 2.6
3		C-123-N-218-I[b] 53 0.8
4		C-113(-S_B-111)-S_A-184-N-218-I[c] 39 2.9 1.5 1.1

a) C, S_B, S_A, N, and I abbreviate crystal, smectic B, smectic A, nematic, and isotropic liquid, respectively. Parentheses and bracket indicate monotropic and virtual transition temperatures, respectively(refer to Fig. 1a). b) Any smectic phase could be observed until the recrystallization occurred at 105 °C. c) The smectic B(hexatic) was assigned according to the method of Gray et al.[1]

corresponding methoxy derivatives(3 and 4) are also indicated for comparison. These hydroxy compounds show a nematic phase, where the nematic-isotropic transition temperatures are nearly equal to those of compounds 3 and 4. This fact indicates that the nematic properties are irrespectve of the hydrogen bond. As we can see from the table, the smectic properties are strongly affected by the substituent. That is, compound 1 has a high S_A-N transition temperature, while the related compound 3 shows only a nematic phase. On the other hand, compound 2 shows no S_A phase. The virtual S_A-N transition temperature extrapolated from Fig. 1a is lower by 19 °C than that of the related compound 4. The order would be quite reasonable, considering the fact that phenol is more polar than anisole.[4] In order to clarify the origin of abnormal smectic properties of compound 1, we examined some binary phase diagrams, as shown in Fig. 1. In Fig. 1a, the N-I transition shows a straight line against the composition of each component. The diagram indicates that compound 2 intrinsically possesses a S_A-N transition at 165 °C.

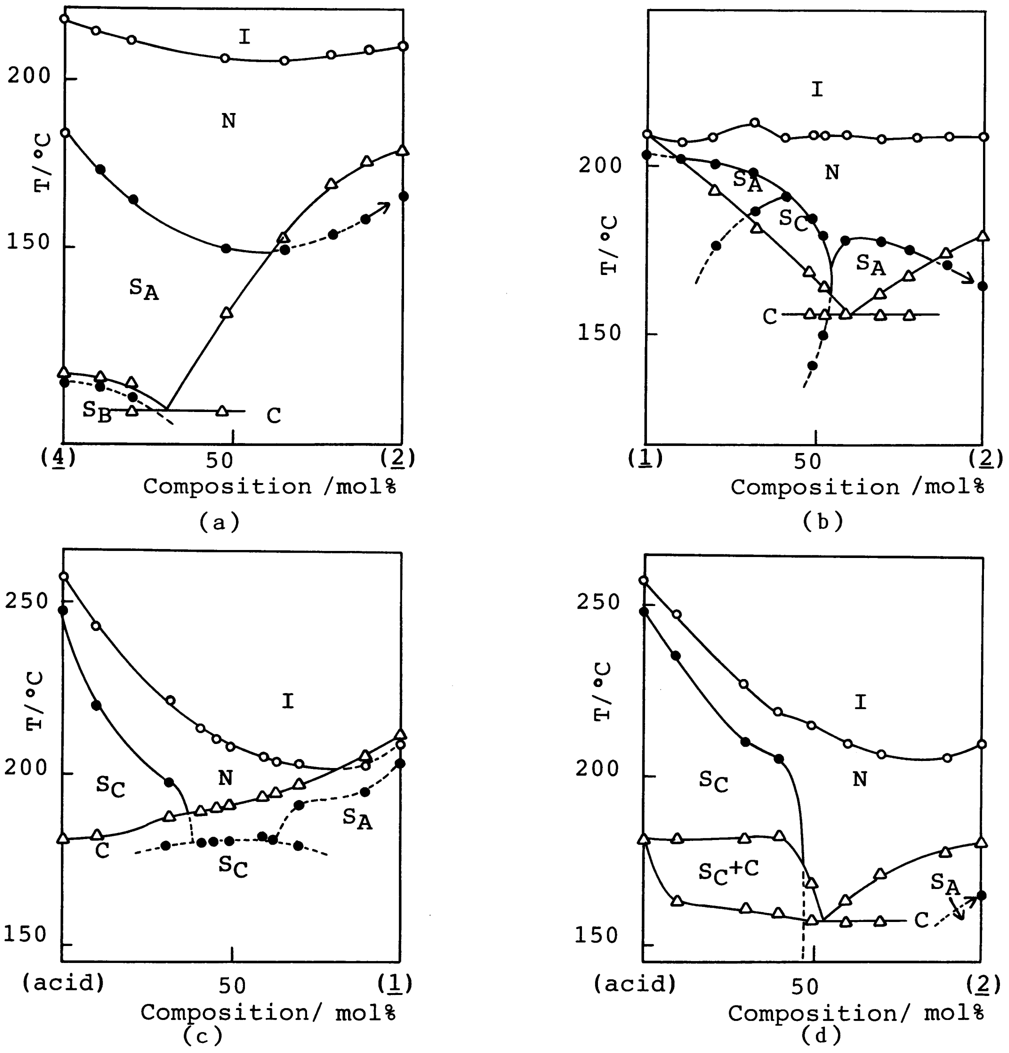


Fig. 1. Binary phase diagrams for the mixtures of: a) 4(on left) and 2(on right), b) 1(on left) and 2(on right), c) 4-octyloxybiphenyl-4'-carboxylic acid(on left) and 1(on right), d) 4-octyloxybiphenyl-4'-carboxylic acid(on left) and 2(on right). Dashed lines indicate monotropic transitions.

In Fig. 1b, the S_A phases of compounds 1 and 2 have no affinity, and a new tilt phase(probably smectic C phase) is induced around the center of the diagram. indicating that both S_A phases have different thermal properties.

In Fig. 1c, the mixture of compound 1 and 4-octyloxybiphenyl-4'-carboxylic acid shows a remarkable downward convexity in the N-I transition, and both S_A-N and smectic C-N transitions are steeply depressed around the center of the diagram. Furthermore, the mixture induces new smectic C phase around the center of the diagram. A similar phase behavior could be observed for the mixture of compound 2 and the acid(Fig. 1d), though the induction of any smectic phase did not occur. The complicating phase behavior should be concerned with the formation of the associated dimer of the acid and phenol:

$$A \rightleftarrows 2A \qquad (1)$$

$$A + B \rightleftarrows AB \qquad (2)$$

where A and B are 4-octyloxybiphenyl-4'-carboxylic acid and compound 1 or 2, respectively. In Fig. 1c, complex AB should be formed and be responsible for the induction of the smectic C phase. The dissociation of the associated acid and phenol results in the steep reduction of smectic A and C thermal stabilities of each component. The situation is different in Fig. 1d. The dissociation of the acid would occur in the liquid crystalline states of the phenol(Eq. 1), reducing the thermal stability of the smectic C phase arising from the acid dimer. However, the induction of any smectic phase does not occur, probably due to the low thermal stability of complex AB, and the reverse reaction of Eq. 1 precedes at low temperature, giving rise to a phase separation in the solid phase. The difference in the thermal properties between compounds 1 and 2, therefore, must arise from the difference in the acidity of both hydroxy groups. The differnce could be recognized in the IR spectroscopy. Compounds 1 and 2 show a sharp absorption band at 3400 cm^{-1} and a broad one in the range between 3600 and 3200 cm^{-1} due to the hydroxy groups, respectively(in the solid phase). The 1:1 mixtures of the acid and compound 1 or 2 also show a similar absorption pattern.

Conclusively, compound 1 forms the associated complex having the remarkable smectic properties. On the other hand, compound 2 does not form such a stable complex. In addition, the dissociation of the aryl acid dimer easily occurs in the phenolic liquid crystal solvents, and the liquid crystalline properties arising from the acid dimer disappear.

References

1) G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals," Heydon & Son Inc., Philadelphia (1984), p. 134, and references cited therein.

2) G. R. Luckhurst and G. W. Gray, "The Molecular Physics of Liquid Crystals," Academic Press, New York (1977), p. 1.

3) D. C. Schroeder ans J. P. Schroeder, J. Org. Chem., 41, 2566 (1976).

4) Y. Sakurai, S. Takenaka, T. Ikemoto, H. Miyake, and S. Kusabayashi, J. Chem. Soc., Perkin Trans. 2, in press.

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