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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hydrogen bonding liquid crystalline benzoic acids with alkylthio groups: phase transition behavior and insights into cybotactic nematic phase

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A simple but novel class of hydrogen bonding liquid crystalline benzoic acids with alkylthio (or alkylsulfanyl; SR) groups was established. In general, although laterally non-substituted rod-like molecules with an alkylthio group are difficult to form some mesophases, the present molecules exclusively form a nematic (N) regime, owing to spontaneous carboxylic dimerization. It was found that the number of carbons in the alkylthio groups strongly correlated with transition temperatures as well as nematogenic stability; odd-even effects. Even-members displayed wider monotropic and enantiortopic N phases, despite the fact that almost all odd-members showed either none or only monotropic-narrower ones. Interestingly, their thermal transition temperatures were lower compared to those for alkoxy (OR) analogues, on account of the small angle (or large bend) of the C–S–C bond as well as the low electron density on their aromatic ring due to the weak electron donor properties of alkylthio groups. Additionally, in-depth wide-angle X-ray diffraction measurements revealed that an alkylthio analogue exhibited significantly enhanced smectic clusters formed in the N regime (or Ncyb phase) as well as the cluster type close to smectic (Sm) A, in comparison with an alkoxy analogue exhibiting a clear SmC-type cluster. The results indicate that a robust S⁺⁺⁺S intermolecular interaction for an alkylthio group into a mesogen affects the kind of smectic cluster in Ncyb phase.

Introduction

Hydrogen bonding (HB) liquid crystalline (LC) (HBLC) molecules attract considerable attention for liquid crystal chemistry as well as supramolecular chemistry. In particular, since the discovery of LC formation with respect to a multiple component system between non-mesogenic pyridine and benzoic acid derivatives, established by Kato et al.,¹ HBLC chemistry has received an even greater attention on not only low-molar mass molecules² but also polymers.³

The most representative and versatile HBLC molecules include benzoic acid derivatives that were first reported around a hundred years ago.⁴ The spontaneous dimerization under ambient conditions, leading to enlarged molecular anisotropy as well as molecular polarizability anisotropy or a dipole moment, can access its LC formation from the melt for its own single-components. Accordingly, several literatures have been reported with respect to the LC properties for benzoic acid derivatives so far.⁵

It is known that benzoic acid derivatives with alkyl and

alkoxy groups display nematic (N) phase and subsequent smectic (Sm) C (SmC) phases corresponding to the alkyl chain length, and that they have smectic clusters containing short-range order in nematic phase (the so called cybotactic nematic phase; N_{cyb} phase).^{5c,i} Since N_{cyb} phase is considered as a key to reveal biaxial nematic phase (N_b),⁶ which is a controversial issue within LC chemistry from the view point of both scientific concerns and applications,⁷ an understanding the LC properties of the benzoic acid derivatives is of great interest. On the other hand, benzoic acid derivatives are vitally important as an ingredient of multi-component HBLCs as stated above as well as a starting material for the synthesis of new organic materials along with organic LC materials.

In our previous report, we focused on the utilization of carboxylic dimerization for diphenyl-acetylene with an alkylthio (or alkylsulfanyl: SR) group, to afford some mesophases.⁸ This is because albeit that an alkylthio group has beneficial effects on optical anisotropy (or birefringenece) due to its high polarizability, it is known that laterally nonsubstituted rod-like molecules with an alkylthio group, as shown in Fig. 1(a), hardly form some mesophases⁹. By incorporating a carboxylic group well-defined enantiotropic mesophases including N phase and a few Sm phases have been induced on account of the hydrogen bond suppressing crystallization ability relative to covalent bonds. Consequently, the following remarkable feature was found: intermolecular S····S interactions derived from alkylthio groups of neighbouring molecules work well even in the most fluid N



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[†]Electronic Supplementary Information (ESI) available: Spectral data, DSC charts, POM images, and X-ray crystal structure analyses. CCDC 1523392. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/x0xx00000x



Fig. 1. Molecular structures of non-mesogenic diphenyl-acetylene with a hexylthio group (a) and mesogenic benzoic acids with alkylthio groups (b).

phase, resulting in enhanced N_{cyb} features compared to an alkoxy derivative.

Based on the context as mentioned above, we speculated that the dimeric forms of benzoic acids [q.v. Fig. 1(b)] could show enhanced cybotactic nematic phase owing to alkylthio groups. To the best of the author's knowledge, the benzoic acids with alkythio groups have not been reported, with the exception of one literature,¹⁰ despite them being the simplest and bottommost molecules. Therefore, their liquid crystallinities or mesophase structures have never been revealed thus far. Its development is highly significant for new HBLC chemistry as well as in the design of subsequent LC materials.

In this study, we present the first report of the detailed mesogenic structures for LC benzoic acids with alkylthio groups. Derivatives with a carbon number of 1–8 were prepared and some molecules successfully formed a well-defined N phase. To clarify the effect of an alkylthio group on not only the mesophase structure but also the crystal structure, derivatives with hexylthio and hexyloxy (viz. the same carbon chain) were in-depth investigated by means of wide angle x-ray diffraction (WAXD) measurement with using each magnetic-aligned specimen as well as single-crystal x-ray diffraction (XRD) measurement.

Experimental

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Materials and methods

4-mercaptobenzoic acid was purchased from TCI and Wako, and 4-hexyloxybenzoic acid and each alkyl halide were purchased from TCI. 4-hexyloxybenzoic acid was recrystallized with methanol purchased from Kanto chemical. Ethanol for the reaction solvent was purchased from Wako. Hydroxyl potassium (KOH) was purchased from Nacalai tesque. The ¹H NMR and ¹³C NMR spectra were measured in CDCl₃ on a JEOL LNM-EX 400 and Avance III 400, respectively, at room temperature using tetramethylsilane (TMS) as an internal standard. FT-IR spectra were measured with a JASCO FT/IR-4200 with KBr (Wako) method. The optical textures were observed by an Olympus BX50 POM with a Linkam LK-600PM hot stage, and the transition temperatures and enthalpies were evaluated by a Shimadzu DSC-60 with heating and Page 2 of 11

cooling scans performed at a rate of 3 °C min⁻¹ under a nitrogen gas. WAXD measurements were conducted using a Bruker D8 DISCOVER equipped with a Vantec-500 detector using Cu-K α radiation. The specimens were kept in glass capillary tubes (1.5 mm diameter) for oriented patterns under a magnetic field (*B* = 1 *T*).



Scheme 1. Synthetic scheme of benzoic acids with alkylthio groups.

Synthesis

All the benzoic acids with alkylthio groups were synthesized according to the Williamson ether reaction as shown in Scheme 1. They are abbreviated as BA–Sm, of which m refers to the carbon numbers in the alkyl chains. As a representative of the synthetic procedure, that of BA–SC6 is depicted below.

4-hexylthio benzoic acid (BA-S6)

A mixture of 4-mercaptobenzoic acid (2.00 g, 13.0 mmol), 1bromohexane (3.22 g, 19.5 mmol), KOH (2.19 g, 39.0 mmol) and ethanol (30 mL) was stirred at reflux temperature for 12h. After the reaction mixture was cooled to room temperature, 2M HCl aq was added into the flask for neutralization until a colorless solid was precipitated. The solid was filtrated and washed with distilled water to afford the target compound. Yield: 95%. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.8 Hz, Ar–H, 2H), 7.31 (d, J = 8.8 Hz, Ar–H, 2H), 3.00 (t, J = 7.2 Hz, S–CH₂, 2H), 1.71 (tt, J = 7.2 and 7.8 Hz, S–CH₂–CH₂, 2H), 1.46 (tt, J = 6.8 and 7.8 Hz, S–(CH₂)₂–CH₂, 2H), 1.39–1.24 (m, (CH₂)₂–CH₃, 4H), 0.89 (t, J = 6.8 Hz, CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 146.0, 130.5, 126.3, 125.6, 32.1, 31.3, 28.7, 28.6, 22.5, 13.9 ppm. FT-IR spectra (KBr) v 2955, 2918, 2872, 2850, 1686, 933 cm⁻¹.

Single crystal data of BA-S6

Representative crystal parameters are shown as follows; Crystal system: monoclinic, space group: C2/c (No. 15), lattice parameters: a = 21.213(12) Å, b = 5.415(3) Å, c = 23.066(12) Å, $\beta = 106.851(9)^{\circ}$, V = 2536(2) Å³, Z = 8, D_{calc} = 1.248 g/cm³, R₁ = 0.0506, wR₂ = 0.1413. The data are deposited on The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif. CCDC 1523392 involves the supplementary crystallographic data for BA–S6.

Results and discussion

FT-IR measurements on solid states

All the BA–Sm and a hexyloxy derivative (BA–O6) were subject to FT-IR measurements in each solid state (KBr) at room temperature. As a representative case, the FT-IR spectra of BA–S6 and BA–O6 are shown in Fig. 2, which are discussed elaborately. We can clearly see three major features for BA–S6



Fig. 2. FT-IR spectra for BA–S6 (solid line) and BA–O6 (dotted line) on KBr method at room temperature.

and BA–O6. Firstly, broad bands at the range from near 2500 to 3500 cm^{-1} are detected. Next, the bands from the stretching vibration of C=O for carboxylic acid are observed at approximately 1680 cm⁻¹. It is known that in the case of alkoxybenzoic acids existing in a monomeric form; in diluted solution, the stretching vibration of C=O for carboxylic acid is observed at 1760 cm^{-1.5i} Finally, the out-of-plane between H and OH wagging vibration bands of carboxylic acid dimers at approximately at 940 cm⁻¹ are taken. Thus, similar trends are observed for all BA–Sm shown in the the ESI. These results establish the dimeric form in the solid state at room temperature for all BA–Sm and BA–O6, as visualized for BA–S6 from its single crystal.

Phase transition behavior

The thermal transition temperatures and enthalpies for each compound are listed in Table 1, which were determined by DSC measurements. The POM images and DSC traces of all the compounds, excluding those for BA-S1 due to sublimation and BA-S6 illustrated in the manuscript, are shown in ESI. Since the sublimation was observed for the short alkyl chain members (BA-S1 and BA-S2), their enthalpies on transitions from the mesophases to isotropic (Iso) phases were not determined. Here, some BA-Sm with relatively long alkyl chains display N phase,10 despite the fact that laterally nonsubstituted rod-like molecules with alkylthio groups seldom form any mesophases as described in the introduction. A representative DSC trace with a POM image for BA-S6 is shown in Fig. 3. It indicates that BA-S6 has enantiortopic N phase evidenced by two transition peaks on both heating/cooling process [Fig. 3(a)] and a schlieren texture with two and four brushes [Fig. 3(b)]. For the sake of clarity, all the phase diagrams as a function of the alkyl carbon number (m) are illustrated in Fig. 4. Upon heating as shown in Fig. 4(a), almost all compounds do not exhibit any mesophases, with the exception of BA-S6 and BA-S8, of which their mesophase ranges are 8.1 and 3.1°C, respectively. Upon cooling as shown in Fig. 4(b), on the other hand, BA-S4 and BA-S7 also form nematic phase, in addition to BA-S6 and BA-S8. N regimes upon cooling for BA-S6 and BA-S8 are apparently expanded

due to the super cooling effect in comparison with those upon heating. In particular, the N range for BA-S6 is the widest value of 25°C among those for all analogues upon cooling, on account of a considerable decrease in the transition temperature from N phase to crystal phase. The above results apparently suggest that mesophases can form more easily be easier to be formed for even-m members compared to odd-m members; odd-even effect to mesogenic incidence. Additionally, Fig. 4(b) illustrates the fidelity in the carbon numbers with respect to transition temperatures from Iso to N phase upon cooling. The temperatures for even-m members are higher than those for odd-m members. These trends are similar to that of alkoxy derivatives^{5a-f} and opposite to that for alkyl derivatives,^{5f,g} due to the additional atom (sulfur or oxygen) between the mesogenic core and the alkyl linkage. A similar fidelity is observed for their enthalpies from Iso to N phase transition upon cooling process. By and large, alkyl chains contribute to mesogenic incidence and stability evidenced by the fact that their mesophases become stable with an increase in alkyl chain length. Notably, the two following distinct features for BA-Sm are observed compared with the alkoxy derivatives in literature.5b,c,e,f Firstly, BA-Sm exclusively display nematic phase even in the long alkyl-chain analog of BA-S8, although alkoxy benzoic acids form SmC phase even on heptyloxy analog. Next, the thermal transition temperatures are apparently lower than those for alkoxy derivatives, which it is consistent with previous reports.^{10,11} As discussed later, we speculated that they could be ascribed to the steric hindrance derived from the small angle (or large bend) of the C-S-C bond relative to the C-O-C bond evidenced by single crystal X-ray analysis as well as the weak electron donor property for SR group leading low electron density on an aromatic ring (or weak intermolecular attractive interaction) compared to an OR group.



Fig. 3. DSC curve at a rate of 3°C min⁻¹ (a) and POM image at 110°C upon cooling for BA–S6 (b).

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Compd.	Cr	Ν						
		Т	ΔН		Т	ΔH		
BA-S1	•	193ª	_b					
		188	_b					
BA–S2		145.5ª	_ ^b					
	•	140.5	_ ^b					
BA–S3		144.7	21.5				•	
	•	114.8	20.8				•	
BA–S4	•	120.8	21.9				•	
	•	110.1	19.9	•	114.3	0.9		
BA–S5	•	113.8	25.2				•	
	•	108.3	24.6				•	
BA–S6	•	103.9	23.7	•	112.0	1.1	•	
	•	86.2	22.6	•	111.1	0.9	•	
BA–S7	•	113.5	28.7				•	
	•	98.6	27.8	•	104.4	0.7	•	
BA–S8	•	106.3	23.5	•	109.5	1.0	•	
		97.6	23.8		108.6	1.1		

Table1. Thermal transition temperatures (7: °C) and enthalpies (ΔH : kJ mol⁻¹) upon

^a Upon first heating.

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^b Not determined due to sublimation.





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WAXD measurements on nematic regimes

In order to elucidate the effect of alkylthio substitution into N phase structures in detail, we carried out WAXD measurements using specimens oriented by applying a magnetic field. For comparison, we employed the derivatives with the same alkyl length of 6, viz. BA-O6 and BA-S6. The 2D-WAXD patterns obtained for BA-O6 and BA-S6 on each N regime are shown in Fig. 5(a) and 5(b), respectively. Two halos in the wide-angle region, corresponding to the diffractions derived from mean lateral intermolecular distance (d_{wax}) , indicate that the molecular long axes on both specimens well oriented along the magnetic field direction represented by arrows. From the diffractions, d_{wax} values were evaluated and their temperature dependence from Iso to N phase is illustrated in Fig. 6, where $T_{\rm IN}$ and T refer to the transition temperature from Iso to N phase, and measurement temperature, respectively. Here, it should be noted that the proximity among lateral molecules appears even in Iso phase for BA-S6 compared to BA-O6. The d_{wax} value of 4.6 Å for BA–S6 is less than 4.7 Å for BA–O6, implying the existence of S...S interaction in Iso phase. In addition, the d_{wax} on N regime for BA–S6 is apparently smaller relative to that of BA–O6 at a range of similar T_{IN} –T. During the course of cooling, the d_{wax} values for both compounds gradually decrease with a decrease in temperature.



Fig. 5. The 2D-WAXD patterns obtained for magnetically aligned specimens of BA–S6 (a) and BA–OC6 (b) on each nematic regime at 95°C. The scan directions to obtain respective 1D-WAXD patterns in small angle regions are described in (c).



Fig. 6. Mean lateral intermolecular distance ($d_{\rm wax}$) for BA–S6 (circle) and BA–O6 (square).

Next, let us discuss the diffractions in each small angle region. As shown in Fig. 5(a), it is clear that four diffused spots split on opposite sides of the meridional line are observed for BA-O6. This result is reminiscent of the existence of smectic C like clusters in the N regime; molecules in each layer tilt against layer normal (the so called cybotactic nematic C phase; N_{cvbC}). As can be seen in Fig. 5(b), whereas, such diffraction split is unclear in a visual manner for BA-S6. In Fig. 7, the scans on the azimuthal angle of the innermost sprit diffractions for both compounds are performed, to estimate the mean tilt angle in the SmC like clusters, $\chi/2$, which are tabulated in Table 2. That for BA-O6 exceeds over a large value of 50° throughout its N regime. By Fig. 7, the diffraction split is visualized for BA-S6 too. However, it is apparently undefined compared to that of BA–O6. The $\chi/2$ values of more or less 40° over a range of N phase for BA-S6 are significantly smaller than those of BA–O6. The reduction of the $\chi/2$ values is thought to be due to the S...S contacts; the intermolecular attractive interaction among the sulfur atoms on neighbouring molecules. These results allow us to speculate that the cluster type in the nematic phase of BA-S6 proceeds to smectic A; molecules in each layer do not tilt against layer normal (the so called cybotactic nematic A phase; N_{cybA}) (vide infra).

In order to verify the speculation, we carried out three typesscans in the small angle region of 2D-WAXD patterns described in Fig. 5(c); a scan along the meridian direction (meridian scan), split direction (diagonal scan) and direction on the azimuthal angle (azimuthal scan). The azimuthal scan includes up to the diffractions in the wide-angle regions. The obtained *d*-spacing, given as $d_{sax}(\text{mer})$, $d_{sax}(\text{dia})$ and $d_{sax}(\text{azi})$ from these diffractions, means the layer spacing is derived from the cluster type of SmA, SmC, and their combinations, respectively. Their temperature dependences for BA–S6 and for BA–O6 also are compiled in Table 2.

When transited from Iso to N phase, d_{sax} (mer) for BA–S6 is 28 Å at 110°C, which is shorter than the dimeric form length of 32 Å evaluated from a single crystal XRD measurement. Then, it clearly increases with a decrease in temperature, and finally is close to the dimeric form length at the lowest N temperature of 95°C. This trend can be explained as follows; at a high temperature on N regime, the nematogenic molecules largely deviate from the nematic director or the direction of the magnetic field, indicative of a low-order parameter. With a

decrease in temperature, the molecular density in the clusters gradually becomes higher. Consequently, the mobility of alkyl chains tends to be disturbed with lowering temperature, leading to the growing d_{sax} (mer). Whereas, the d_{sax} (dia) for BA–S6 seem mostly unchanged within nematic temperatures, contrary to the d_{sax} (mer).

With respect to BA–O6 forming clear N_{cybC} phase, d_{sax} (dia) soakingly changes from 21 to 19 Å with a decrease in temperature. This temperature dependence is similar to that of SmC phase, in which the molecular tilt against layer normal becomes larger with a lowering temperature. While, d_{sax} (mer) exhibits a nearly molecular dimeric form length of 32 Å over a



Fig. 7. Azimuthal profiles of the diffraction of the small angle region for BA–S6 (bottom solid line) and BA–O6 (top dotted line).

Table 2. WAXD profile parameters for each small angle region on temperature dependence for BA–S6 and BA–O6.

	T (°C) –	d _{sax} (Å)				χ/2	
Compd.		(azi)	(mer)	(dia)	I _{sax} /I _{wax} "	(°)	
BA-S6	95	28.4	31.9	23.7	1.8	45	
	98	27.4	31.2	23.2	1.7	44	
	101	27.4	30.4	23.4	1.6	42	
	104	26.8	29.7	24	1.5	42	
	107	26.5	29.1	24.5	1.4	40	
	110	25.2	28.4	24.2	1.2	38	
	116 ^b	21.7	-	-	0.8	-	
BA-06	100	19.8	31.7	19.1	1.3	53	
	105	20.0	31.7	19.3	1.3	53	
	115	20.9	31.2	19.6	1.2	52	
	130	22	31.5	20.1	1.2	52	
	140	22.7	30.5	20.3	1.2	51	
	149	23	29.5	20.9	1.1	51	
	160 ^b	19.4	-	-	0.8	-	

^a Evaluated from the scans on the azimuthal line (azimuthal scans).

^b Isotropic phase.

DOI: 10.1039/C7NJ00282C Journal Name

range of N regime and are nearly unchanged. The $d_{sax}(mer)$ for BA-O6 may imply the diffraction from transitionally formed SmA like clusters or free molecules.

For the purpose of clarity, additionally, the 1D-WAXD patterns obtained from azimuthal scans for BA-S6 and BA-O6 are shown in Fig. 8. As can be seen in Fig. 8(a), the diffraction maxima on the small angle region for BA-S6 gradually shifts to a smaller angle of 2θ with decreasing temperature, indicating that diffraction for the meridian scan is superior to that for the diagonal scan. The temperature dependence of 2θ shift is similar to smectic A phase. That is to say, N_{cvbA} propensity could be predominant for BA-S6 but transitionally synchronous with N_{cvbC} evidenced by the fact that an undefined



Fig. 8. The temperature dependences of the 1D-WAXD patterns for BA–S6 (a) and BA–O6 (b).

split was detected. On the other hand, the diffraction maxima for BA–O6 apparently moves to wide angle of 2θ , reflecting the $N_{cybC}\ due$ to the temperature dependence of the SmC like cluster in the N phase.

From the view point of the diffraction intensity ratio between the small angle region (I_{sax}) and the wide-angle halo (I_{wax}) , (viz. $I_{\text{sax}}/I_{\text{wax}}$), their cybotactic nematic tendency was evaluated. The temperature dependence for each compound is summarized in Table 2 and Fig. 9. It is noteworthy that the $I_{\text{sax}}/I_{\text{wax}}$ for BA–S6 increases more steeply than that for BA–O6

with decreasing temperatures, until it finally reaches the high value of 1.8. Generally, it is known that normal nematogenic molecules display $I_{sax}/I_{wax} < 1.^{12}$ The results mean that shortrange positional correlations are strongly enhanced for BA-S6 due to S...S interactions. Although BA-O6 also exhibits relatively high values ($I_{sax}/I_{wax} \approx 1.2$), it is only slightly temperature dependent over the entire mesophase range.

On the other hand, it is known that a magnetic field greatly influences nematic-phase behavior.13 Therefore, we performed the WAXD measurement for both specimens without a magnetic field, too. The obtained 1D-WAXD patterns for both molecules are shown in supporting information. It is estimated that the I_{sax}/I_{wax} values are 1.3 for BA–S6 at 101°C and 1.0 for BA-O6 at 115°C. These results indicate that BA-S6 and BA-O6 exhibit N_{cvb} phase in the case without magnetic field, too, and that an alkylthio group has a beneficial effect in enhanced N_{cvb} phase compared to an alkoxy group, which is consistent with the results obtained under the condition with magnetic field. In addition, comparing the values with and without a magnetic field for both molecules, the former is apparently larger than the latter, indicating that the magnetic field enhanced cybotactic nematic tendency.

Throughout the above WAXD investigations into benzoic acids with hexylthio and hexyloxy groups, we can safely explain the effects of a sulfur atom on rod-like nematogenic molecules, and offer a probable molecular arrangement in their Sm clusters as shown in Fig. 10. The S····S attractive interactions work well even in fluid phases so that alkylthio groups



Fig. 9. The temperature dependences of I_{sax}/I_{wax} values for BA–S6 (circle) and BA–O6 (square).

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contribute to not only the strongly enhanced cybotactic nematic phase but also the tendency for Sm A like cluster formations in the N phase, explained by an increase in the I_{sax}/I_{wax} value and reduced tilt angle compared with those for an alkoxy analog.

XRD measurement for a single crystal of BA-S6

Single crystals of BA-S6 were obtained by recrystallization from methanol solution, and a single crystal XRD measurement was carried out to afford the molecular packing structure in the crystal phase as shown in Fig. 11. Firstly, the geometries for molecular packing are argued. Fig. 11 visualizes the dimeric forms by hydrogen bond for BA-S6. The hydrogen bond distance in the dimers (viz. the dimeric distance between C=O····H-O) of 1.66 Å is the usual value for conventional carboxylic dimers. In marked contrast with the crystal molecules,14 structures for various sulfur-containing unexpectedly, S...S contacts close to S atoms in the lateral molecules are not observed in the crystal packing for BA-S6.



Fig. 11. Molecular packing in the unit cell of BA-S6.

Whereas, apparent $CH^{\dots\pi}$ interaction between laterally phenyl rings of neighbouring molecules are noticed. It was assumed that the $CH^{\dots\pi}$ interaction that took place between lateral molecules could predominantly work during the crystallization process as an alternative to S^{...}S interaction. Based on Ref. [15] and our measurement, on the other hand, the single crystal

BA–O6 displays O···O contacts, and molecules are packed in parallel with each other on the phenyl ring plane in contrast with BA–S6 molecules.

Next, the geometries of each single molecule are discussed. The crystal lattice for BA-O6 contains six independent molecules,¹⁶ in which a similar result was obtained with our measurements as well. While, it was found that BA-S6 has molecules with single geometry in the lattice. With respect to the comparison of the dihedral angles between the mean plane of aliphatic chains and that of aromatic rings, BA-O6 exhibits six values between 1.0° and 6.0°, and BA-S6 shows a single value of 4.8°, indicating that the dihedral angles are nearly unchanged with each other. On the other hand, the bond angles of C-S-C at the base of the phenyl ring for BA-S6 of 104.7° are much smaller than mean for those of C-O-C for BA-O6 (approximately 120°), indicative of a large bend for an alkylhthio group. Such a large bend of an alkylthio group could have steric hindrance to lead to the three following specific features for rod-like molecules with alkylthio groups compared to alkoxy counterparts; intrinsically poor liquid crystallinity, relatively low transition temperatures and nematogenic propensity. Furthermore, it was reported that the rotation barrier of an alkylthio group is lower than that of alkoxy group, which also supports the above features.¹⁶

Hammett constants and chemical shifts of aromatic protons

In addition, the intrinsically poor liquid crystallinity and relatively low-transition-temperature phenomena and nematogenic propensity observed for rod-like molecules with alkylthio groups reported so far could also be thought to be due to the electron density on an aromatic ring. According to the empirical Hammett constants, which means the electron donating and accepting properties for benzoic acid derivatives, those for SMe, SEt and OMe at para-positions are 0.00, 0.03 and -0.27, respectively.¹⁷ These values suggest that alkylthio groups at para-positions for benzoic acids have no or significantly weak donating properties, while alkoxy groups have an apparently electron-donating property. That is, it suggests that although the former hardly affects the electron density on an aromatic ring, the latter renders an aromatic ring electron-rich. Our results on ¹H NMR characterizations are definitely in good agreement with the consideration of the Hammett constants. The chemical shifts derived from two species of protons on an aromatic ring are 7.98 and 7.31 for BA-S6, and 8.05 and 6.93 for BA-O6, respectively. So, that means the aromatic protons are well shielded for BA-O6 compared to BA-S6. In other words, an alkylthio group at a para position leads less electron density on an aromatic ring than an alkoxy group, resulting in weak CH··· π and/or π ··· π intermolecular interactions. These results allow us to speculate that not only a small angle of C-S-C bonding (or a large bend) but also less electron density on an aromatic ring contribute to intrinsically poor liquid crystallinity and relative-low transitiontemperature phenomena as well as nematogenic propensity for rod-like molecules with alkylthio groups, compared to alkoxy counterparts.

3

Conclusions

In this article, we describe the first report of the detailed liquid crystallinity of hydrogen bonding LC benzoic acids with alkylthio groups. Some BA-Sm displayed nematic phase owing to hydrogen bonding dimerization. Their nematic temperatures are lower than those for alkoxy counterparts.

Based on the WAXD measurement for BA-S6 and alkoxy BA-O6, it was found that BA-S6 exhibited enhanced N_{cvb} phase with a predominant N_{cvbA} propensity relative to BA-O6 exhibiting clear N_{cvbC} phase, on account of the intermolecular S....S interaction.

The single crystal XRD measurements revealed a larger bend for C-S-C than C-O-C. In addition, Hammett constants and chemical shifts of aromatic protons suggested that electron density on an aromatic ring for BA-S6 is lower than that for BA-O6, speculating that the CH- π and/or π - π intermolecular interactions are lower for BA-S6 than for BA-O6. The above results, including the small angle of C-S-C and the low electron density on an aromatic, could be able to contribute to the following distinct features for rod-like molecules with an alkylthio group compared to conventional alkoxy counterparts; (1) intrinsically poor liquid crystallinity, (2) relatively low phase transition temperature, and (3) nematogenic tendency.

These findings are beneficial in providing fundamental insights into molecular structure-mesophase relations for hydrogen-bonding liquid crystalline materials as well as novel molecular designs based on sulfur-containing, rod-shaped LC materials.

Acknowledgements

This work was partly supported by JSPS KAKENHI Grant number 15H06285, and research grants from The Nitto Foundation and The Toukai Foundation for Technology. The authors thank Prof. Masatoshi Tokita for WAXD measurements.

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A novel class of hydrogen bonding liquid crystalline benzoic acids with alkylthio groups was established and their phase transition behavior was investigated in detail.



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