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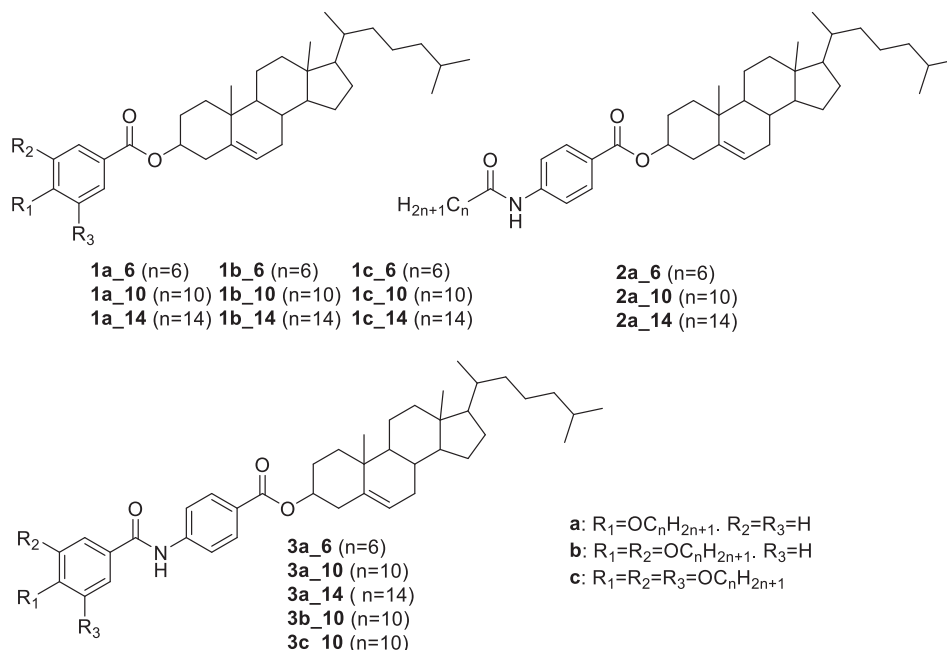
Synthesis, Crystal Structure, and Properties of Cholesteryl 4-(Benzoylamino)benzoate Derivatives

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Abstract:—As a new liquid crystalline organogelator, cholesteryl 4-(benzoylamino)benzoate derivatives were prepared. Cholesteryl 4-(benzoylamino)benzoate derivatives had enantiotropic cholesteric and chiral smectic C phases. The crystals of cholesteryl 4-(4'-hexyloxybenzoylamino)benzoate had a layer structure with intermolecular $\pi \cdots \pi$, C-H $\cdots \pi$, and C-H $\cdots$ O interaction such as smectic C phase. Furthermore cholesteryl 4-(4'-alkoxybenzoylamino)benzoate gelled organic liquid such as *n*-decane, *n*-hexadecene, 1-butanol, 1-hexanol, 1-decanol, toluene, salad oil, linalool, geraniol, nerol, citronellol, limonene, linalyl acetate, lavender oil, orange oil, and lemon oil. The terpene gels show good release the volatile components for a long period.

1. Introduction

Self-assembled systems are of great importance, particularly for their potential application to nanomaterials such as liquid crystals and gelators.¹⁻⁴⁾ Many studies have been reported on their structure and mechanisms of molecular aggregation. More than 110000 liquid crystalline compounds are reported till now.⁵⁾ To design a liquid crystalline molecule, a rigid core and flexible alkyl side chains are required.⁶⁾ The number of organogelators has rapidly increased over the last 20 years.¹⁻³⁾ In the past, new organogelators were often discovered accidentally, and the studies were dedicated to understanding the relationship between the structure of a gelator and its gelation behavior. The aggregation of organogelators into fibrous networks is driven by multiple weak interactions such as dipole-dipole, van der Waals, hydrogen-bonding, and π -stacking interactions. Gelators are commonly classified by their driving force for molecular aggregation: nonhydrogen-bond-based and hydrogen-bond-based gelators. Amide compounds such as amino acid and urea and hydroxy compounds such as 12-hydroxystearic acid and sugars are hydrogen-bond-based gelators, whereas anthracene, cholesterol, and tropone derivatives are nonhydrogen-

Fig. 1. Chemical structures of **1-3**.

bond-based gelators. Recently, we have reported several liquid crystalline organogelators called “organogelling liquid crystal.”⁷⁻¹⁰⁾ Several organogelling liquid crystals, octa-alkoxy-substituted α -diketonato copper complex,¹¹⁾ octa(dodecyl)tetrapyrzazino-porphyrzazine,¹²⁾ 3,4,5-trialkoxybenzene derivatives,^{9, 13-22)} triphenylene derivatives,^{10, 23-25)} dibenzophenazine derivatives,^{26, 27)} hydrazine derivatives,²⁸⁻³⁰⁾ 4-cyanophenyl 4-*n*-alkoxybenzoates,¹⁰⁾ 4-cyano-4'-alkoxybiphenyls,¹⁰⁾ 4,4'-dialkanoyloxybiphenyls,¹⁰⁾ azoxybenzene derivatives,¹⁰⁾ coumarin derivatives,^{31, 32)} aroylhydrazone derivatives,³³⁾ cholesteryl alkanooate derivatives,^{10, 34-38)} cholesteryl benzoates (**1**),⁷⁾ and 4-(alkanoylamino)benzoates (**2**)³⁹⁾ have been reported. However, **1** and **2** could not be used for gel preparation at low concentration. In this paper, we report the crystal structure, mesomorphic and gelation properties of cholesteryl 4-(benzoylamino)benzoates (**3**)⁴⁰⁾ as the new liquid crystalline organogelators with cholesteryl benzoate and hydrogen-bonding groups and its application to terpene and perfume gels.

2. Experimental

2.1. Analysis

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. The melting points were obtained using a Yanagimoto micro-melting-point apparatus. The NMR spectra were recorded using JEOL GSX-270 spectrometer and solutions in $CDCl_3$ at

room temperature; the chemical shifts are expressed in δ units. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 6200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K α radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

2.2. Synthesis of Cholesteryl 4-(benzoylamino)benzoates (3)

A mixture of 4-(4'-hexyloxybenzoylamino)benzoic acid (0.740 g, 2.17 mmol), cholesterol (0.802 g, 2.07 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC $\cdot$ HCl) (0.424 g, 2.21 mmol), and 4-dimethylaminopyridine (DMAP) (0.275 g, 2.25 mmol) in THF (15 cm³) was stirred at room temperature for 12 hr. The mixture was poured into water, and organic matter was extracted with chloroform. The organic layer was dried over Na₂SO₄. The organic layer was evaporated in vacuo to leave a residue, which was chromatographed in chloroform on a silica-gel column to give crystals. The crystals were recrystallized with hexane-ethyl acetate (1:2 *v/v*) to give colorless crystals (**3a_6**, 0.710 g, 46%).

3a_6: ¹H NMR (270.05 Hz, CDCl₃) δ =0.69 (3H, s), 0.87 (6H, d, *J*=6.6 Hz), 0.92 (3H, d, *J*=6.6 Hz), 1.07 (3H, s), 0.85-2.03 (37H, m), 2.47 (2H, d, *J*=7.9 Hz), 4.03 (2H, t, *J*=6.6 Hz), 4.84 (1H, m), 5.42 (1H, d, *J*=3.9 Hz), 7.05 (2H, d, *J*=8.9 Hz), 7.72 (2H, d, *J*=8.6 Hz), 7.84 (2H, d, *J*=8.9 Hz), 7.85 (1H, s), and 8.05 (2H, d, *J*=8.6 Hz). Found: C, 79.42; H, 9.48; N, 1.95%. Calcd for C₄₇H₆₇NO₄: C, 79.50; H, 9.51; N, 1.97%.

3a_10 (49%): ¹H NMR (270.05 Hz, CDCl₃) δ =0.69 (3H, s), 0.86 (3H, d, *J*=6.6 Hz), 0.87 (3H, d, *J*=6.6 Hz), 0.92 (3H, d, *J*=6.6 Hz), 1.07 (3H, s), 0.85-2.05 (45H, m), 2.47 (2H, d, *J*=7.6 Hz), 4.02 (2H, t, *J*=6.6 Hz), 4.84 (1H, m), 5.42 (1H, d, *J*=3.9 Hz), 6.97 (2H, d, *J*=8.9 Hz), 7.72 (2H, d, *J*=8.9 Hz), 7.84 (2H, d, *J*=8.9 Hz), 7.86 (1H, s), and 8.05 (2H, d, *J*=8.9 Hz). Found: C, 79.64; H, 9.86; N, 1.79%. Calcd for C₅₁H₇₅NO₄: C, 79.95; H, 9.87; N, 1.83.

3a_14 (45%): ¹H NMR (270.05 Hz, CDCl₃) δ =0.69 (3H, s), 0.87 (6H, d, *J*=6.9 Hz), 0.92 (3H, d, *J*=6.6 Hz), 1.07 (3H, s), 0.85-2.03 (53H, m), 2.47 (2H, d, *J*=7.9 Hz), 4.02 (2H, t, *J*=6.6 Hz), 4.85 (1H, m), 5.42 (1H, d, *J*=3.9 Hz), 6.97 (2H, d, *J*=8.6 Hz), 7.72 (2H, d, *J*=8.9 Hz), 7.84 (2H, d, *J*=8.6 Hz), 7.85 (1H, s), and 8.06 (2H, d, *J*=8.6 Hz). und: C, 80.40; H, 10.18; N, 1.67%. Calcd for C₅₅H₈₃NO₄: C, 80.34; H, 10.17; N, 1.70%.

3b_10 (51%): ¹H NMR (270.05 Hz, CDCl₃) δ =0.69 (3H, s), 0.86 (3H, d, *J*=6.7 Hz), 0.87 (3H, d, *J*=6.7 Hz), 0.92 (3H, d, *J*=6.6 Hz), 1.05 (3H, s), 0.85-2.04 (64H, m), 2.47 (2H, d, *J*=7.9 Hz), 4.06 (2H, t, *J*=6.6 Hz), 4.07 (2H, t, *J*=6.6 Hz), 4.83 (1H, m), 5.42 (1H, d, *J*=3.6 Hz), 6.91 (1H, d, *J*=8.2 Hz), 7.37 (1H, dd, *J*=2.0 and 8.2 Hz), 7.47 (1H, d, *J*=2.0 Hz), 7.71 (2H, d, *J*=8.6 Hz), 7.87 (1H, s), and 8.05 (2H, d, *J*=8.6 Hz). Found: C, 79.28; H, 10.41; N, 1.48%. Calcd for C₆₁H₉₅NO₅: C, 79.43; H, 10.38; N, 1.52%.

3c_10 (38%): ^1H NMR (270.05 Hz, CDCl_3) δ =0.69 (3H, s), 0.86 (3H, d, J =6.6 Hz), 0.86 (3H, d, J =6.6 Hz), 0.92 (3H, d, J =6.3 Hz), 1.05 (3H, s), 0.85-2.04 (86H, m), 2.45 (2H, d, J =7.6 Hz), 3.96 (4H, t, J =6.6 Hz), 3.99 (2H, t, J =6.6 Hz), 4.81 (1H, m), 5.38 (1H, d, J =4.3 Hz), 7.05 (2H, s), 7.74 (2H, d, J =8.9 Hz), 8.01 (2H, d, J =8.6 Hz), and 8.31 (1H, s). Found: C, 78.95; H, 10.83; N, 1.25%. Calcd for $\text{C}_{71}\text{H}_{115}\text{NO}_6$: C, 79.06; H, 10.75; N, 1.30%.

2.3. Mesomorphic properties of **3**

The transition temperatures were measured by differential scanning calorimetry (Seiko DSC6200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered $\text{Cu-K}\alpha$ radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

2.4. X-ray crystallographic analysis of **3a_6**

Single crystals of **3a_6** for X-ray analysis were grown in a chloroform and methanol solution (1:1 v/v) at room temperature. A colorless prism crystal of CHNO having approximate dimensions of 0.200x0.120x0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-RAPID imaging plate area detector with graphite monochromated $\text{Cu-K}\alpha$ radiation (λ =1.54187 Å). The data collection and cell refinement: *CrystalClear*. Data reduction: *CrystalStructure 4.0*; program used to solve structure: *SIR2008*; program used to refine structure: *SHELXL97*; Molecular graphics: *Mercury 3.3*. All H atoms were positioned with idealized geometry and were refined isotropic (U_{iso} (H)=1.2 U_{eq} (C)) using a riding model with C-H=0.95 Å for aromatic H atoms, C-H=0.98 Å for methyl H atoms, C-H=0.99 Å for methylene H atoms, and C-H=1.00 Å for methine H atoms. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication and deposition number 2076412.

Crystal data for **3a_6**: $\text{C}_{47}\text{H}_{67}\text{NO}_4$, monoclinic, $C2$, a =34.475 (9) Å, b =5.811 (2) Å, c =20.598 (5) Å, β =93.25 (2)°, V =4120 (2) Å³, Z =4, M_r =710.05, D_x =1.145 Mg m^{-3} , μ =5.501 cm^{-1} , T =113 (1) K, refinement on F^2 (*SHELXL97*), R [$F^2 > 2\sigma(F^2)$]=0.0524, wR (F^2)=0.1226, S =0.909.

2.5. Gelation of organic liquids with **3**

Cholesteryl 4-(benzoylamino)benzoates (**3**) (100 mg) were weighted accurately into a screw cap vial. An amount of 1.0 cm^3 organic liquid (n -hexane, n -decane, n -hexadecane, cyclohexane, methanol, ethanol, 1-butanol, 1-hexanol, 1-decanol, ethyl acetate, acetonitrile, THF, benzene,

toluene, salad oil) was added. The screw cap of the vial was closed and heated at 120°C until a clear solution was obtained. The vial was left at 25°C in an incubator for one hour. The gelation was considered successful when upon inversion there was no fluid running down the walls of the vial.

2.6. Preparation of terpene and perfume gels and releasing test of volatile components

Cholesteryl 4-(4'-decyloxybenzoylamino)benzoate (**3a_10**) (5.5-6.8 mg) were weighted into a screw cap vial. An amount of 1.0 cm³ terpene (linalool, geraniol, nerol, citronellol, limonene, linalyl acetate) or essential oil (lavender oil, lemon oil, orange oil,) was added. The screw cap of the vial was closed and heated at 120°C until a clear solution was obtained. The vial was left at 25°C in an incubator for one hour. The release tests of the volatile components from **3a_10**-limonene, linalool, linalyl acetate, lemon oil, and lavender oil gels were employed. The caps of the glass tubes containing the fragrance gel opened. They were left at room temperature and their weight were measured after 10, 20, 50, 100 and 200 days.

3. Result & Discussion

3.1. Synthesis

Cholesteryl 4-(benzoylamino)benzoates (**3**) were prepared by the esterification of cholesterol with the corresponding 4-(benzoylamino)benzoic acid in the presence of EDC · HCl and DMAP. The structures and purities of the compounds (**3**) were ascertained by NMR spectroscopy and elemental analyses.

3.2. Mesomorphic properties

The transition temperatures and thermal behaviors of **3** were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage and an X-ray diffraction study. The optical micrographs of chiral smectic C (SmC*) phase and cholesteric (N*) phase of **3_14** were shown in Fig. 2. Chiral smectic C and cholesteric phases were determined from a following observation and an X-ray diffraction study, i.e., broken focal-conic fan, banded focal-conic fan, and schlieren textures for chiral smectic C phase;⁴¹⁾ Grandjean steps at the border and oily streak textures for the cholesteric phase. The thermal behaviors of the cholesteryl benzoates (**1-3**) are summarized in Table 1.

Compounds (**3a** and **2a**) had a phase sequence of Cr-SmC*-N*-Isotropic (Iso), whereas **1** had a phase sequence of Cr-SmA-N*-Iso.⁷⁾ The melting and clearing points of **3** were higher than those of the corresponding derivatives (**1**, **2**).^{7, 39)} This means that the addition of the benzoylamino group strengthen the intermolecular interactions. However cholesteryl 4-(3',4'-didecyloxybenzoylamino)

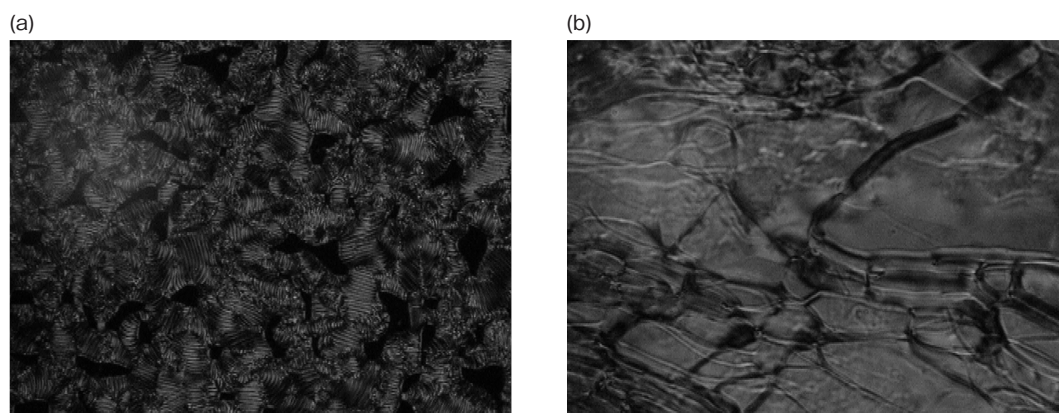


Fig. 2. Optical cross-polarizing micrographs of **3a_14** at (a) 225°C (SmC*) and (b) 245°C (N*). All pictures taken on cooling from the isotropic phase.⁴⁰⁾

Table 1. Transition temperatures (°C) of **3**⁴⁰⁾

Compounds	n	Transition Temperatures/°C
3a_6	6	Cr · 231.4 · N* · 301.7 · Dec
3a_10	10	Cr · 216.1 · SmC* · 254.1 · N* · 264.4 · Iso
3a_14	14	Cr · 201.4 · SmC* · 239.4 · N* · 246.6 · Iso
3b_10	10	Cr · 175.7 · Iso
3c_10	10	Cr · 93.4 · Iso

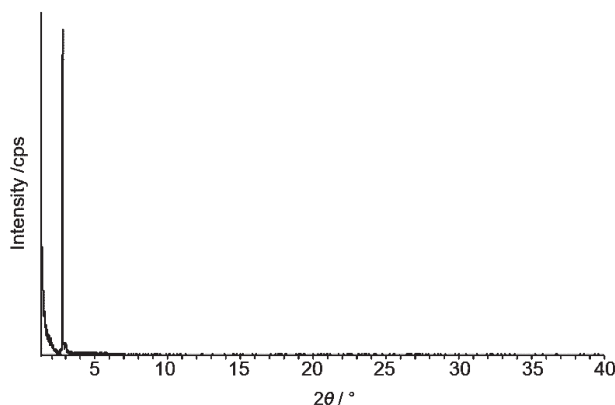
Cr: Crystals, N*: Cholesteric Phase, SmC*: Chiral Smectic C Phase, Iso: Isotropic Liquid.

benzoate (**3b_10**) and cholesteryl 4-(3',4',5'-tridecyloxybenzoylamino)benzoate (**3c_10**) were not mesomorphic. The melting and clearing points of **3b_10** and **3c_10** were lower than that of 4-(4'-decyloxybenzoylamino)benzoate (**3a_10**).

We measured the XRD pattern of the mesophases. The XRD pattern of compound **3a_14** measured at 230°C showed only one sharp reflection at $2\theta=2.90^\circ$ (corresponding to 30.5 Å) as shown in Fig. 3. The smectic layer spacings (d) and molecular lengths (l) of **3a** are listed in Table 2. The molecular lengths (l) of **3a** were calculated by the MM2 method. The d/l ratios of chiral smectic C (SmC*) phase of **3a** are 0.73 for **3a_10** and 0.69 for **3a_14**, respectively. This result suggests that the molecular long axes of **3a** are tilted at 47° for **3a_10** and 44° for **3a_14**, respectively, with respect to the normal to the layer in the SmC* phase and form the layer.

3.3. X-ray crystallographic analysis

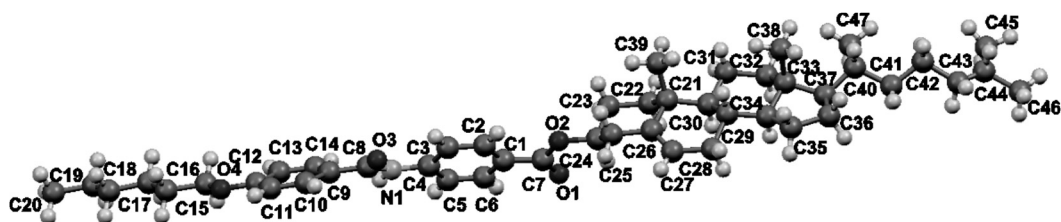
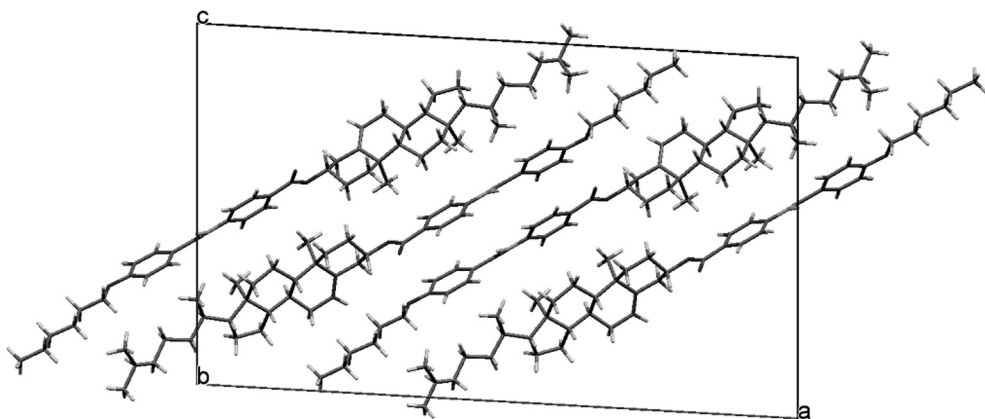
Elucidation of crystal structures and investigation of physical properties of LCs are important for studying the relationship between molecular structures and mesophases. Numerous studies have been dedicated to the structural investigation and the determination of the molecular

Fig. 3. XRD pattern of **3a_14** at 230°C.⁴⁰⁾Table 2. Layer spacings (Å) and molecular lengths (Å) of **3**⁴⁰⁾

Compounds	Temperatures/°C	Layer Spacings/Å	Molecular Lengths/Å	<i>d/l</i>	Tilt Angle/°
3a_10	220	30.5	41.7	0.73	47
3a_14	230	32.3	46.5	0.69	44

aggregation mechanisms. X-ray crystallographic analysis plays an important role to obtain the information about intermolecular interactions controlling mesophases. We have also reported the crystal structures of some LCs such as bis(tropon-2-yl)-4,4'-azobisbenzoate,⁴²⁾ 4,4'-dimethoxy-2,2'-dihydroxybenzalazine,⁴³⁾ and cholesteryl 4-(7-diethylamino-2-oxo-2*H*-1-benzopyran-3-yl) benzoate.⁴⁴⁾ Good correlations have been found between the crystal structures and liquid crystalline behaviours of the LCs. The structure of **3a_6** was confirmed by X-ray crystallographic analysis with the aim of contributing to a deeper understanding of the relationships between mesomorphic property and molecular packing in the crystal structure. A view of the molecular structure of **3a_6** is shown in Fig. 4.

The molecular length of **3a_6** is 36.703 (6) Å for the C20 ... C46 distance. The hexyl chain has an all-*trans* conformation, thus forming an almost planar *zigzag* chain; the deviation of atoms from the least-squares plane defined by atoms C15/C16/C17/C18/C19/C20 is within 0.070 (3) Å. The two benzene rings are twisted for the central amide group. The dihedral angles between the least-squares plane A (defined by C1/C2/C3/C4/C5/C6) and B (defined by C9/C10/C11/C12/C13/C14), between the least-squares A and C (defined by N1/H1/O3/C8), and between the least-squares B and C are 42.6 (1)°, 19.1 (2)°, and 23.8 (1)°, respectively. The dihedral angle between the phenyl ring A and carboxyl group (defined by C7/O1/O2) is 2.8 (1)°. The dihedral angle between the carboxyl group and fused cyclohexane ring (defined by C21/C22/C23/C24/C25/C26) of cholesterol is 58.6

Fig. 4. Molecular structure of **3a_6**.Fig. 5. Packing diagram of **3a_6** viewed down the *b* axis.

(1)^o, is similar to that (56.0 (1)^o)⁽⁴⁵⁾ of cholesteryl benzoate. Compound has a tilted layer structure as shown in Fig. 5. The crystal structure is consistent with the packing model in the smectic C phase. An intermolecular $\pi \cdots \pi$ interaction between the cholesteryl 4(benzoylamino)benzoate dimer planes is observed. The distance between intermolecular 4(benzoylamino)benzoate planes is 3.494 (5) Å for C2 $\cdots$ C10ⁱ [symmetry code: (i) -x, y, 1-z], which is within the range associated with $\pi \cdots \pi$ interactions (3.3-3.8 Å).⁽⁴²⁾

There are intermolecular C-H $\cdots$ π and C-H $\cdots$ O interactions as shown in Fig. 6 and Table 3. The distance between H47C and the centroid (Cg^v) [symmetry code: (v) 1/2-x, 1/2 + y, 1-z] of benzene ring (defined by C9/C10/C11/C12/C13/C14) is 3.036 Å, which is similar to the intermolecular C-H $\cdots$ π interaction [3.079 Å]⁽⁴⁴⁾ of cholesteryl 4-(7-diethylamino-2-oxo-2H-1-benzopyran-3-yl) benzoate. For C-H $\cdots$ O interaction, The H5 $\cdots$ O3ⁱⁱ [symmetry code: (ii) x, y-1, z] distance is 2.461 Å, which agrees with typical C-H $\cdots$ O distance (2.5-2.8 Å).^(43, 44) No intermolecular N-H $\cdots$ O interaction is observed in crystals. The molecules form a tilted layer structure via intermolecular $\pi \cdots \pi$, C-H $\cdots$ π , and C-H $\cdots$ O interaction.

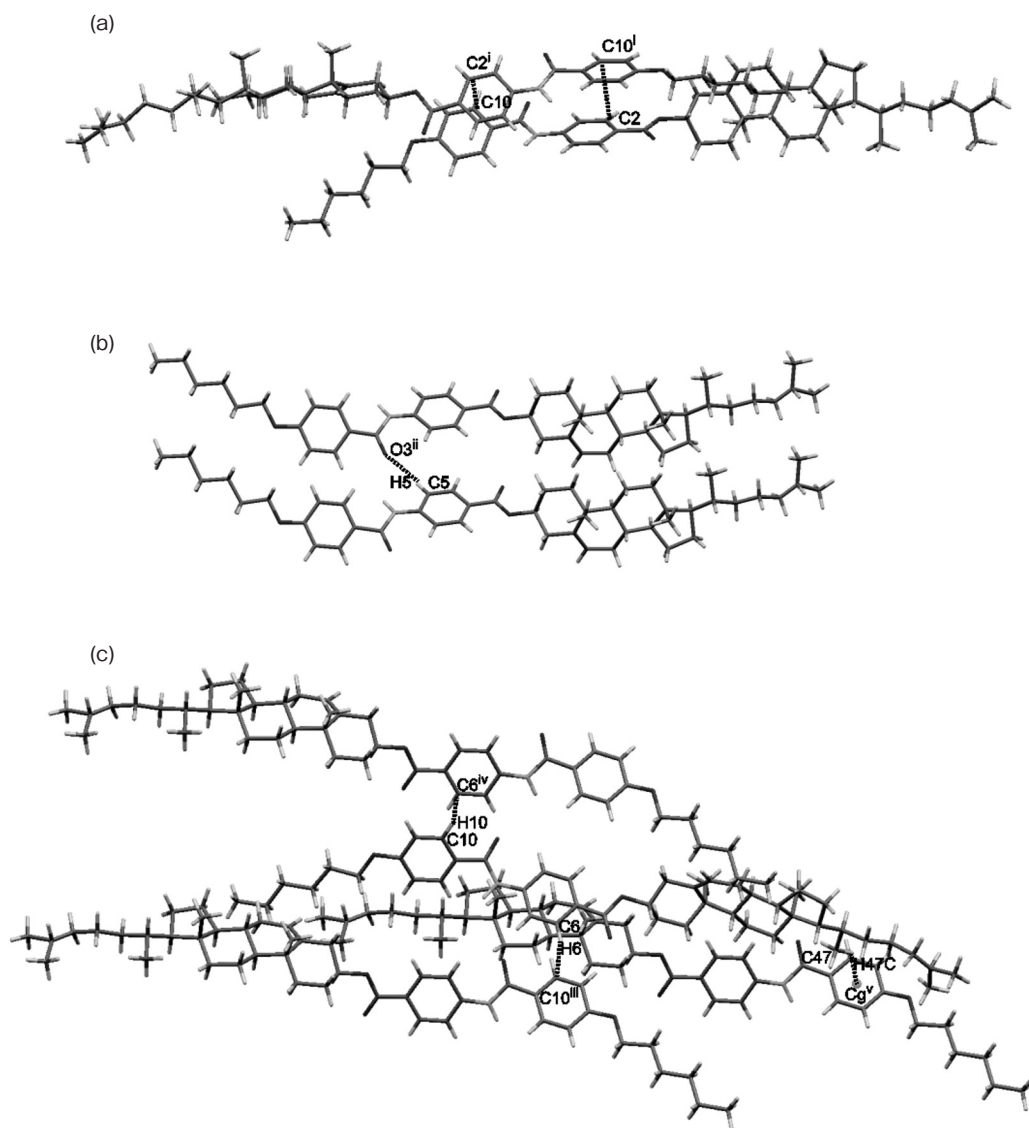


Fig. 6. Intermolecular (a) $\pi \cdots \pi$, (b) $\text{C-H} \cdots \text{O}$, and (c) $\text{C-H} \cdots \pi$ interactions of **3a_6** (indicated by broken line). Symmetry codes: (i) $-x, y, 1-z$, (ii) $x, y-1, z$, (iii) $-x, y-1, 1-z$, (iv) $-x, y+1, 1-z$, (v) $1/2-x, 1/2+y, 1-z$. The centroid atom (Cg) of the benzene ring (C9/C10/C11/C12/C13/C14) was generated.

Table 3. Intermolecular $\text{C-H} \cdots \pi$ and $\text{C-H} \cdots \text{O}$ interactions of **3a_6**

D	H	A	D-H	H $\cdots$ A	D $\cdots$ A	D-H $\cdots$ A	Symmetry code
C5	H5	O3 ⁱⁱ	0.950	2.461	3.296 (5)	147	(ii) $x, y-1, z$
C6	H6	C10 ⁱⁱⁱ	0.950	2.843	3.623 (5)	140	(iii) $-x, y-1, 1-z$
C10	H10	C6 ^{iv}	0.950	2.818	3.623 (5)	143	(iv) $-x, y+1, 1-z$
C47	H47	Cg ^v	0.980	3.036	3.723 (6)	128	(v) $1/2-x, 1/2+y, 1-z$

3.4. Gelation properties

We carried out the gelation test of **3** in various organic solvents (*n*-hexane, *n*-decane, *n*-hexadecane, cyclohexane, methanol, ethanol, 1-butanol, 1-hexanol, 1-decanol, ethyl acetate, acetonitrile, THF, benzene, toluene, and salad oil). The result of the gelation test with **3** is shown in Table 4. Compounds (**3**) gelled *n*-decane, *n*-hexadecane, 1-butanol, 1-hexanol, 1-decanol, toluene, and salad oil, while **1** gelled 1-decanol and *n*-hexadecane and **2** gelled 1-decanol.

Fig. 7 shows the photograph of **3a_10**-decanol gel and an optical micrograph of the gel phase of **3a_10** in 1-decanol (0.9 w/v%) recorded at 25°C on cooling from an isotropic liquid state. Highly intertwined, rod-like fibers aligned to form the network structures by making bundles with diameters of ca. 1.4 μm . The minimum gel concentrations (MGC, g/dm³) of **3a** are 40 for **3a_6** · *n*-hexadecane, 4 for **3a_10** · *n*-hexadecane, 49 for **3a_14** · *n*-hexadecane, 4 for **3a_6** · 1-decanol, 3 for **3a_10** · 1-decanol, and 4 for **3a_14** · 1-decanol. The gelation abilities of **3a_10** for 1-decanol and *n*-hexadecane are superior than those of the other cholesteryl benzoates (**1** and **2**).^{7, 39)}

Table 4. Gelation ability of **3**⁴⁰⁾

	3a_6	3a_10	3a_14	3b_10	3c_10
<i>n</i> -Hexane	Insol	Insol	Insol	Cryst	Sol
<i>n</i> -Decane	Gel	Gel	Gel	Cryst	Sol
<i>n</i> -Hexadecane	Gel (40)	Gel (4)	Gel (49)	Gel (73)	Cryst
Cyclohexane	Insol	Insol	Insol	Cryst	Cryst
Methanol	Insol	Insol	Insol	Cryst	Cryst
Ethanol	Insol	Insol	Insol	Cryst	Cryst
1-Butanol	Gel	Gel	Gel	Gel	Cryst
1-Hexanol	Gel	Gel	Gel	Gel	Cryst
1-Decanol	Gel (4)	Gel (3)	Gel (4)	Gel (60)	Cryst
Ethyl acetate	Insol	Insol	Insol	Cryst	Cryst
Acetonitrile	Cryst	Cryst	Cryst	Cryst	Cryst
THF	Cryst	Cryst	Gel	Sol	Sol
Benzene	Cryst	Cryst	Cryst	Cryst	Sol
Toluene	Cryst	Gel (14)	Gel (16)	Gel (50)	Sol
Salad oil	Gel	Gel	Gel	Gel	Cr

Gel: Gelation, Cryst: Crystallization, Insol: Insoluble, Sol: Solution.

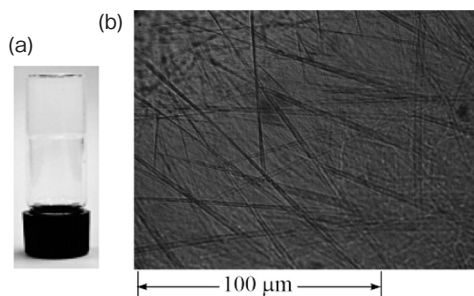


Fig. 7. (a) Photograph and (b) micrograph of **3a_10** · 1-decanol gel.⁴⁰⁾

3.5. Preparation of terpene and perfume gels

To study the application of organogelator **3a** to new materials, terpene and perfume gels were prepared. In perfume, fragrance and deodorant materials, hydrogelators such as carrageenan, agar, collagen, gellan gum, and gelatin, etc. have been used for gelations of water-containing terpenes, essential oils, and perfumes. Therefore, the purity of the oils in the gels is low and most of the components of these materials comprise water. Fortunately, under the gel-organic liquid conditions (5.5-6.8 mg/1.0 cm³), **3a_10** could gel the terpenoids such as linalool, geraniol, nerol, citronellol, limonene, linalyl acetate and essential oils such as lavender oil, lemon oil, orange oil as shown in Fig. 8. The release tests of the volatile components from **3a_10**-limonene, linalool, linalyl acetate, lemon oil, and lavender oil gels were carried out. The caps of the glass tubes containing the fragrance gel were opened. They were left to stand at room temperature, and the weight changes of the gels and neat liquids were investigated, as shown in Table 4. The weights of the gels and neat liquids decreased with time. The rate of decrease in the weight of the gels were

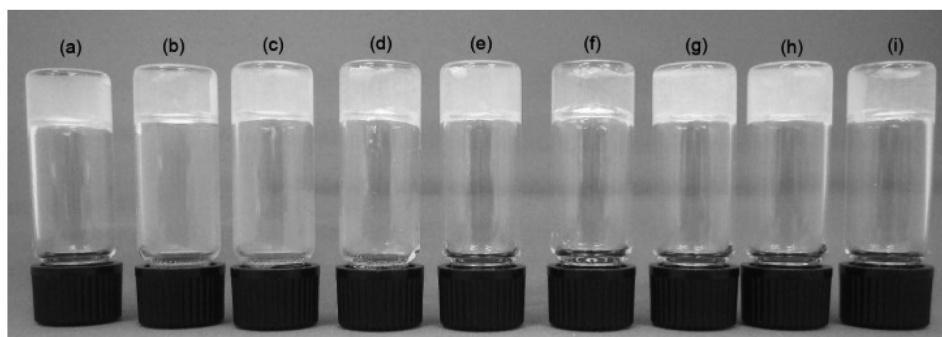


Fig. 8 Photograph of (a) **3a_10**·linalool, (b) **3a_10**·geraniol, (c) **3a_10**·nerol, (d) **3a_10**·citronellol, (e) **3a_10**·limonene, (f) **3a_10**·linalyl acetate, (g) **3a_10**·lavender oil, (h) **3a_10**·lemon oil, and (i) **3a_10**·orange oil gels.⁴⁰⁾

Table 5. Weight changes (mg) of the terpene gels containing **3a_10** and neat liquids by release tests of the volatile components

Solvents/Status	3a_10 /mg	Weight/mg					
		0	after 10d	after 20d	after 50d	after 100d	after 200d
Limonene/Gel	6.4	827.6	730.4	653.6	434.8	283.1	266.0
Limonene/Liquid		825.2	722.1	641.7	436.7	323.4	305.6
Linalol/Gel	6.1	849.3	842.6	835.2	814.1	787.2	709.1
Linalol/Liquid		855.3	848.0	841.7	825.5	807.0	723.8
Linalyl acetate/Gel	6.8	872.0	866.1	862.5	852.0	841.0	820.2
Linalyl acetate/Liquid		872.2	864.8	860.7	848.9	830.2	797.8
lemon oil/Gel	6.3	855.2	750.1	663.5	409.3	202.6	188.5
lemon oil/Liquid		862.7	758.3	668.7	403.4	188.2	183.0
lavender oil/Gel	5.5	934.8	920.6	913.9	896	873.5	827.1
lavender oil/Liquid		932.2	920.2	918.7	904.4	885.8	838.8

similar to those of neat liquids, showing that the gel state controlled the release of the volatile components. After 200 day, each gel maintained the gel state with a characteristic scent of terpenoids.

4. Conclusion

Cholesteryl 4-(4'-decyloxybenzoylamino)benzoate (**3a_10**) had enantiotropic chiral smectic C and cholesteric phases. The molecules of **3a_6** form layer structures with intermolecular $\pi \cdots \pi$, C-H $\cdots \pi$, and C-H $\cdots$ O interaction. Furthermore cholesteryl 4-(4'-alkoxybenzoylamino)benzoates had a good gelation ability for organic liquid such as *n*-decane, *n*-hexadecene, 1-butanol, 1-hexanol, 1-decanol, toluene, salad oil. We succeeded preparing perfume gels containing 99% or more of terpene and essential oil. The terpene gels showed good release the volatile components for a long period. The gels may be utilized as fragrance and deodorant agents.

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