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Properties of 2-Acetyl-7-nonylfluorene and Its O-Analogs in the Alkyl Chain

Yutaka Takabayashi, Toshiyuki Fukami,
Atsushi Yamamoto, Takao Kimura, and
Masahiro Minabe*

Department of Applied Chemistry, Faculty of Engineering,
Utsunomiya University, Yoto 7-1-2, Utsunomiya 321-8585

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The O-analog in the alkyl chain of 2-acetyl-7-nonylfluorene is less stable than the parent compound concerning the mesophase as a liquid crystal, except for 2-acetyl-7-(octyloxy)fluorene.

Some of liquid crystals contain the fluorene moiety as a core.[1—3] Fluorene differs from biphenyl due to the existence of a 9-methylene bridge. This results in the two six-membered rings being fixed to each other in the same plane, and each of the 2- and 7-substituents deviating from the axis of the central 4a–4b bond. The structure of fluorene has both merit and demerit concerning the liquid crystallinity, compared with that of biphenyl.[3,4] The merit of fluorene is the delocalization of π-electrons over the biphenyl moiety due to the coplanarity of the molecule. This is expected to increase the thermal stability of the mesophase, because of increasing polarity of the core part. A demerit of fluorene is that the methylene group increases the width of the molecule. In addition, the substituents at the 2- and 7-positions are not situated in a mutually linear manner, and the molecule is thus a "banana shape".[5,6] These demerits decrease the thermal stability of the mesophase.

A previous paper of ours concerned the liquid crystallinity of 2-acyl-7-[*p*-(alkoxy)benzylideneamino]fluorenes in comparison with that of biphenyl derivatives.[3] Fluorene derivatives show a mesophase over a wider range of temperature than that of the biphenyl series. The introduction of an acetyl group results in an elevation of the melting point in the case of fluorene derivatives.

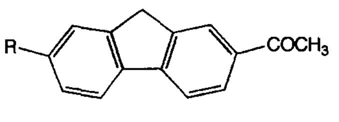
A lowering of the melting point should be caused by the insertion of an oxygen atom in the side chain of the liquid crystal, while a systematic comparison has scarcely been studied. For example, 4-cyano-4′-[2-(methoxy)ethoxy]biphenyl shows a lower melting point and a higher cleaning point than those of 4-butoxy-4′-cyanobiphenyl.[7]

This paper deals with the stability of the mesophase of 2-acetyl-7-nonylfluorene (**1**) and the O-analogs in the nonyl moiety (Scheme 1). This is planned in order to design a stable liquid crystal at a low temperature using fluorene as a core, because that fluorene is expected to increase the thermal stability of the mesogen. Regarding this study, 2-acetyl-7-(octyloxy)fluorene (**2**) has been reported as a liquid crystal.[8]

2-Acetyl-7-[2-(pentyloxy)ethoxy]- (**3**), -7-[5-(ethoxy)pentyloxy]- (**4**), 7-{2-[2-(ethoxy)ethoxy]ethoxy}- (**5**), -7-[(heptyloxy)methyl]- (**6**), and -7-[2-(hexyloxy)ethyl]fluorene (**7**) were synthesized in addition to **1** and **2**. Table 1 gives the thermal behavior of **1**—**5**. The phase-transition temperature at the heating process was determined using a DSC and a microscope. The enthalpy change was estimated from the endothermic curves on DSC.

The lowering clearing point of **1** compared to **2** indicates that a lack of polar phenolic oxygen atom is ineffective for the mesophase.[1,2] The substitution of a methylene group in the octyl moiety of **2** by an oxygen atom causes less stability of the mesophase than that of **2**. The properties of **3** and **4**, being similar to that of **1**, mean that introducing of oxygen as alkyl alkyl ether cancels the effect of the phenolic oxygen of **2**. The insertion of an oxygen atom into **3** gives **5**, showing a property similar to that of **3**. In the cases of **6** and **7**, the mesophase completely disappears upon the substitution of a methylene group in the nonyl moiety of **1** by an oxygen atom.

The oxygen–methylene bond is in the same plane with the fluorene moiety in the case of **2**, as shown in Fig. 1. The corresponding angle in **1** is nearly orthogonal as the most stable conformation, while the energy barrier of the rotation is as low (< 1.1 kcal) as the molecules being packed mutually to form a liquid crystal. The oxygen atom must be located between the aryl and alkyl groups, but not between



1: $R = (CH_2)_8CH_3$

2: $R = O(CH_2)_7CH_3$

3: $R = O(CH_2)_2O(CH_2)_4CH_3$

4: $R = O(CH_2)_5OCH_2CH_3$

5: $R = O(CH_2)_2O(CH_2)_2OCH_2CH_3$

6: $R = CH_2O(CH_2)_6CH_3$

7: $R = (CH_2)_2O(CH_2)_5CH_3$

Scheme 1.

Table 1. Phase-Transition Temperature of Compds, **1**—**7**

Compd	Temp$^{a)}$ / °C
1	C-(54[10.8]-S$^{b)}$)-81[34.3]-I
2	C-96[15.2]-S_A-107[2.7]-I
3	C-(52[1.2]-S_A)-77[12.2]-I
4	C-(73[1.9]-S_A)-78[34.7]-I
5	C-(51[1.5]-S_A)-79[9.3]-I
6	C-56[20.2]-I
7	C-64[24.0]-I

a) At heating process. b) Kind of phase is uncertain at present. ( ): Monotropic transition at cooling process. C: Crystal phase; S: smectic phase; I: isotropic phase. [ ]: Enthalpy change (kJ mol^{-1}).

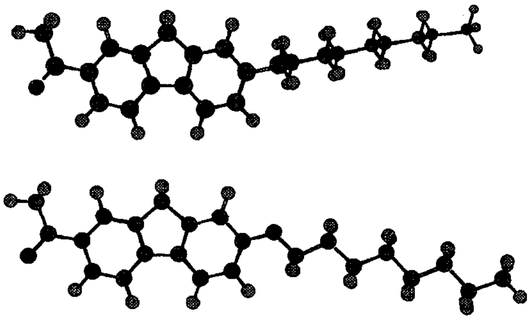


Fig. 1. Molecular models of **1** (upper) and **2** (lower) as the most stable conformer.

the alkyl and alkyl groups. The oxygen atom as a part of the alkyl alkyl ether increases the free rotation of both alkyl groups, resulting in a decrease of the overall dipole moment of the aggregate of molecules. On the other hand, the free rotation between the aryl group and oxygen in alkyl aryl ether is restricted because of the resonance effect; therefore, the dipole moment due to the oxygen is held in the direction along the aryl plane of the molecule.[9]

Experimental

The melting points (Table 1) are uncorrected. The NMR spectra (0.7 ml $CDCl_3$) were recorded with a Varian VXR-300. The mass and elemental analyses were measured with a JMX-AX 500 (JEOL) and an EA 1108 CHNS-O (Fison Instruments), respectively. These date gave satisfactory results. The DSC curves were obtained with a Rigaku DSC 8230. Table 1 shows the second trial of repeated records of the DSC curves. The conformation of molecules was estimated using a molecular mechanics program Chem 3D pro (Cambridge Soft Corp.).

2-Acetyl-7-nonylfluorene (1). To a mixture of 2-nonylfluorene (290 mg, 1 mmol) in carbon disulfide (5 ml) was added anhydrous $AlCl_3$ (170 mg, 1.3 mmol) and the whole was stirred. Acetyl chloride (0.09 ml, 1.2 mmol) was dropped to the mixture for 10 min with ice-cooling, and the resulting mixture was stirred for 20 min. After the usual treatment, the crude product was recrystallized from EtOH to give **1** (310 mg, 96%).

2-Acetyl-7-(octyloxy)fluorene (2).[8] A mixture of 2-fluorenol (727 mg, 4 mmol), 1-bromooctane (1.0 ml, 5.8 mmol), and potassium carbonate (520 mg, 4 mmol) in DMF (28 ml) was refluxed under an atmosphere of argon for 28 h to give 688 mg (59%) of 2-(octyloxy)fluorene: Mp 76—78 °C (from hexane). Acylation of 2-(octyloxy)fluorene with $AlCl_3$ and AcCl in dichloromethane afforded **2** in a 47% yield (from hexane) (lit,[8] mp 98—108.5 °C).

2-Acetyl-7-[2-(pentyloxy)ethoxy]fluorene (3). A mixture of 7-acetyl-2-fluorenol (455 mg, 2 mmol), 1-chloro-2-(pentyloxy)ethane (462 mg, 3.1 mmol), and potassium carbonate (285 mg, 2.1 mmol) in DMF (10 ml) was refluxed under an atmosphere of argon for 24 h to afford 321 mg (47%) of **3**.

2-Acetyl-7-[5-(ethoxy)pentyloxy]fluorene (4). Using a procedure similar to that mentioned above, the reaction of 7-acetyl-2-fluorenol and 1-ethoxy-5-chloropentane gave **4** in a 56% yield.

2-Acetyl-7-{2-[2-(ethoxy)ethoxy]ethoxy}fluorene (5). Similarly, **5** was obtained by the reaction of 7-acetyl-2-fluorenol and 1-[2-(ethoxy)ethoxy]-2-chloroethane in a 16% yield.

2-Acetyl-7-[(heptyloxy)methyl]fluorene (6). The acetylation of methyl fluorene-2-carboxylate afforded methyl 7-acetylfluorene-2-carboxylate in 85% yield: Mp 184—186 °C (from ethanol). A mixture of the methyl ester, ethylene glycol, and TsOH in benzene was gently refluxed with the separation of water for 6 h. Upon neutralization of the sulfonic acid with potassium carbonate, the solution was chromatographed on alumina with benzene to give an 89% of methyl 7-(2-methyl-1,3-dioxolan-2-yl)fluorene-2-carboxylate: Mp 156—159 °C (from cyclohexane).

The reduction of the acetal ester with lithium aluminum hydride in ether and treatment with dilute sulfuric acid gave 7-acetylfluorene-2-methanol in an 80% yield: Mp 156—158 °C (from ethanol). The methanol was converted with thionyl chloride to 2-acetyl-7-(chloromethyl)fluorene (73%): Mp 110—113 °C (from cyclohexane). Sodium was added to 1-heptanol, and the mixture was stirred with the chloride mentioned above at 60 °C for 10 min. Upon the usual treatment, 52% of **6** was obtained.

2-Acetyl-7-[2-(hexyloxy)ethyl]fluorene (7). Methyl fluorene-2-acetate was acylated by a method similar to that mentioned above, giving methyl 7-acetylfluorene-2-acetate in a 90% yield: Mp 117—120 °C (from ethanol); IR 1735, 1675 cm^{-1}; MS *m*/*z* 280 (M^+). The acetyl group was protected as the corresponding acetal: 83% yield; mp 108—110 °C (from cyclohexane); IR 1735 cm^{-1}; MS *m*/*z* 324 (M^+). The reduction of the acetal by a method similar to that mentioned above gave 2-(2-hydroxyethyl)-7-(2-methyl-1,3-dioxolan-2-yl)fluorene in a 95% yield: Mp 133—135 °C (from cyclohexane); MS *m*/*z* 296 (M^+).

A mixture of sodium 7-(2-methyl-1,3-dioxolan-2-yl)fluorene-2-ethoxide, 1-bromohexane, benzyltrimethylammonium chloride, and potassium iodide in benzene was refluxed for 48 h, giving acetal of **7**. The acetal was treated with concentrated sulfuric acid in ether with ice-cooling to afford 13% of **7**: IR 1680 cm^{-1}; ^{1}HNMR δ = 0.87 (3H, t, J = 6.9 Hz), 1.22—1.40 (6H, m), 1.57 (2H, qui, J = 6.9 Hz), 2.65 (3H, s), 2.98 (2H, t, J = 7.2 Hz), 3.45 (2H, t, J = 6.9 Hz), 3.67 (2H, t, J = 7.2 Hz), 3.92 (2H, s, H_9), 7.28 (1H, dd, J = 8.1, 1.5 Hz, H_6), 7.46 (1H, d, J = 1.5 Hz, H_8), 7.76 (1H, d, J = 8.1 Hz, H_5), 7.79 (1H, d, J = 8.1 Hz, H_4), 7.99 (1H, dd, J = 8.1, 1.5 Hz, H_3), 8.12 (1H, d, J = 1.5 Hz, H_1); MS *m*/*z* 336 (M^+). Found: C, 81.98; H, 8.36%. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39%.

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