Synthesis of Novel Liquid-Crystalline Thiophene Derivatives and Evaluation of Their Photoresponsive Behavior

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Received February 10, 1997[⊗]

Novel liquid-crystalline (LC) thiophene derivatives were synthesized, and their LC behavior and photoresponsive behavior were explored. Among the thiophene derivatives synthesized, 4-(4-alkylphenylazo)phenyl 2-thienylacrylates (**TAn**, $n = 4$, 5, 6, and 7) were found to show nematic (N) phase. **TAn** exhibited the N phase only when the azobenzene moiety in the molecule was in the trans form while no LC phase when the azobenzene was in the cis form. Photoirradiation of **TA6** in a cell to bring about the trans−cis isomerization of the azobenzene moiety resulted in disappearance of the N phase. The N phase was restored when the irradiated sample was kept in the dark. Time-resolved measurements by means of a laser pulse (355 nm; 10 ns fwhm) revealed that in transmission-mode analysis the N-isotropic phase transition was completed in 8 ms, while in reflection-mode analysis it occurred in 100 μs.

Introduction

Much attention has been paid to photonics in place of electronics with the development of the information society. The essential process of photonics is to control light by light as a stimulus, and in fact many attempts have been made to develop materials for photonics with ultrafast response. Liquid crystals (LCs) have been most extensively used as active media in such applications as color television and display devices for word processors. In these applications, the orientation of LC molecules, usually nematic (N) LCs, is changed by external electric field applied across the LC cells, and contrast is produced between the area where the electric field is applied and the area where no electric field is applied. However, response of NLCs to the change in the electric field is slow (>several milliseconds), which limits the use of LCs as photonic materials for which much faster response is necessary.

It has already been realized that introduction of photoresponsive moieties into LCs is a useful method to provide the LC materials with photoresponsive properties,[1] and it has been demonstrated that when LCs containing azobenzene derivatives are irradiated to cause trans−cis photoisomerization, nematic−isotropic (N−I) phase transition is induced.[2] This phenomenon can be explained in terms of molecular structure of the photoresponsive guest molecules: the trans forms of the azobenzene moiety are favorable to stabilize the LC phase, while the cis forms are bent and unfavorable for the LC phase. The trans−cis photoisomerization of the azobenzene moieties in the NLC phase results in disorganization of the phase structure and induces the N−I phase transition isothermally. Furthermore, we have achieved 200-μs photoresponse of NLCs by the use of photochromic LCs in which the photochromic moiety (azobenzene) plays both roles of a mesogen and a photosensitive moiety.[3] In the azobenzene LCs, the N phase was observed only when the azobenzene moiety was in the trans form, and no LC phase was observed at any temperature when it was in the cis form. So the trans−cis photoisomerization in these LCs resulted directly in disappearance of the N phase.

Thiophene derivatives have been used widely as conducting materials which are chemically more stable than other aromatic compounds.[4] In particular, 2,5-thienylene derivatives are structurally planar and electrically conducting. The use of π-conjugated polymers and oligomers stimulated wide interest in recent years for molecular electronic, photonic, and electroluminescent devices.[5] Whereas polythiophene derivatives provide a wide variation in conjugation length and structural disorder, conjugation length and chemical structure of oligothiophene derivatives have allowed a deep understanding of the parameters controlling the charge-transport and electrical and/or optical properties of the conjugate materials.[6] X-ray structural characterization of these oligomers and conformational analysis with quantum mechanical methods have revealed that structural order is a key parameter.[7,8] Although the electrical and structural properties of the thiophene

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

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S0897-4756(97)00082-3 CCC: $14.00

derivatives have been extensively explored, little work has been performed on their photoresponsive properties with the aim at development of photonic materials by using electron polarization of π-conjugated units. Since photoexcitation brings about ultrafast electron polarization within a few hundreds of femtoseconds,[9] high-performance photonic devices may be constructed by means of the π-conjugated materials which exhibit significant difference in electronic properties between the ground and the excited states.

In this study, we synthesized novel thiophene derivatives with the aims at preparation of liquid-crystalline thiophene derivatives for photonic materials, and explored their photoresponsive behavior.

Experimental Section

Materials. All materials were purchased from Tokyo Kasei Co. and used without further purification except for tetrahydrofuran (THF) which was purified using benzophenone and sodium under argon atmosphere.

Synthesis of Thiophene Derivatives. 2,5-Thienylene derivatives show molecular planarity, but unlike 1,4-phenylene derivatives they are not rodlike but bent. It has been recognized in general that molecules which show LC behavior possess a rodlike core in central part of a molecule.[10] This means that the 2,5-thienylene moiety as the center of the core is not favorable. By reference to the literatures on LC thiophene derivatives,[11] we performed molecular design of the LC thiophene derivatives for photonics in which 2,5-thienylene moiety constitutes the rigid core part, but not the center of the core: 5-(4-octylphenyl)-5′-cyanobithienyl, **CTn**, 2-nitro(or

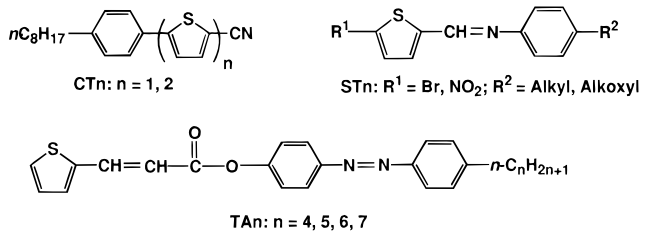
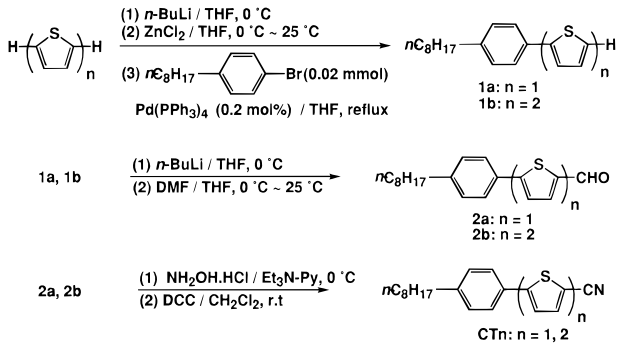


Figure 1. Structure of thiophene derivatives used in this study.

Scheme 1. Synthesis of CTn



bromo)-5-[(4-alkyl(or 4-alkoxyl)phenyliminomethyl]thiophene (**STn**), and 4-(4-alkylphenyl)diazenylphenyl 3-(2-thienyl)propenoate (**TAn**) as shown in Figure 1.

Preparation of CTn. CTn was synthesized following the route shown in Scheme 1.

2-(4-Octylphenyl)thiophene (1a). In a well-dried flask, dry THF (10 mL) and thiophene (0.504 g, 6.01 mmol) were placed, and the mixture was cooled in an ice bath. To this solution, butyllithium (1.66 M hexane solution; 3.62 mL, 6.01 mmol) was added, and the mixture was stirred for 1 h at 0 °C to prepare 2-lithiothiophene. Vacuum-dried zinc chloride (0.800 g, 60.1 mmol) dissolved in dry THF (10 mL) was added to the 2-lithiothiophene solution at 0 °C, and the resulting solution was warmed to room temperature and stirred for 20 h. To a solution of tetrakis(triphenylphosphine)palladium (2.4 mg, 0.02 mmol) and 4-octylbromobenzene (1.61 g, 6.01 mmol) in dry THF (10 mL), the 2-thiophene zinc chloride solution was added, and the resulting mixture was heated to reflux for 15 h. After the reaction mixture was cooled to room temperature, 1 M HCl aqueous solution was added, the mixture being neutralized with $NaHCO_3$ solution, and the product was extracted with diethyl ether. The crude product was purified by column chromatography on silica gel (hexane, $R_f = 0.6$) to give **1a** as a yellow-green oil (0.79 g, 49% yield). ^{1}H NMR δ 0.91 (3H, t, $J = 6.8$ Hz, $-CH_3$), 1.23−1.42 (10H, m, $-(CH_2)_5CH_3$), 1.52−1.72 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.56 (2H, t, $J = 7.6$ Hz, $CH_2(CH_2)_6CH_3$), 6.94 (1H, dd, $J = 3.5$ Hz, 0.9

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Hz, Th-4-H), 7.00 (1H, dd, J = 4.7 Hz, 0.9 Hz, Th-3-H), 7.08 (2H, d, J = 8.0 Hz, Be-3-H, 5-H), 7.19 (1H, dd, J = 3.5 Hz, 4.7 Hz, Th-5-H), 7.35 (2H, d, J = 8.4 Hz, Be-2-H, 6-H). Anal. Calcd for $C_{18}H_{24}S$: C, 79.41; H, 8.82; S, 11.76. Found: C, 79.45; H, 8.89; S, 11.76.

5-Formyl-2-(4-octylphenyl)thiophene (2a).[12] Under an argon atmosphere, **1a** (0.720 g, 2.65 mmol) was dissolved in dry THF (4 mL), and to this solution was added butyllithium (1.67 M hexane solution; 1.90 mL, 3.18 mmol) dropwise at 0 °C with stirring. After 1 h, this solution was added to a THF solution (4 mL) of dimethylformamide (0.240 g, 3.18 mmol) at 0 °C, and the mixture was gradually warmed to room temperature and left with stirring for 16 h before quenching with 1 M HCl aqueous solution. The mixture was neutralized with $NaHCO_3$ and extracted with diethyl ether. The crude product was purified by column chromatography on silica gel (hexane/chloroform = 6/1, R_f = 0.45), and a yellow solid of **2a** was obtained (0.351 g, 45% yield). Mp 76−79 °C. ^{1}H NMR δ 0.90 (3H, t, J = 6.9 Hz, $-CH_3$), 1.22−1.42 (10H, m, $-(CH_2)_5CH_3$), 1.51−1.72 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.55 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_6CH_3$), 7.06 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.19 (1H, d, J = 3.4 Hz, Th-3-H), 7.39 (2H, d, J = 8.0 Hz, Be-2-H, 6-H), 7.62 (1H, d, J = 3.4 Hz, Th-4-H), 9.65 (1H, s, −CHO). Anal. Calcd for $C_{18}H_{24}SO$: C, 76.00; H, 8.00; S, 10.67. Found: C, 75.96; H, 7.92; S, 10.87.

5-Cyano-2-(4-octylphenyl)thiophene (CT1).[13] A solution of triethylamine (52.0 mg, 0.52 mmol) in dry dichloromethane (2 mL) was added to a solution of **2a** (0.151 g, 0.50 mmol) in dry pyridine (2 mL) containing a trace amount of cupper(II) sulfate·$5H_2O$ under argon atmosphere. The mixture was then added to a solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC; 12.1 mg, 0.561 mmol) in dry dichloromethane (8 mL) at 25 °C, and the reaction mixture stirred for 2 h. Formic acid (0.05 mL) was added to the mixture, and the residue was chromatographed on silica gel with dichloromethane as an eluent. The product was finally purified by recrystallization from a mixture of benzene and hexane (6/1 vol/vol). **CT1** was obtained as a yellow solid (94 mg, 64% yield). Mp 93 °C. ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.22−1.43 (10H, m, $-(CH_2)_5CH_3$), 1.51−1.73 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.55 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_6CH_3$), 7.05 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.19 (1H, d, J = 3.4 Hz, Th-3-H), 7.36 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.52 (1H, d, J = 3.4 Hz, Th-4-H). IR (KBr, cm^{-1}) 2980, 2270, 1740, 1700, 1560, 1500, 1460, 1140, 800. Anal. Calcd for $C_{18}H_{23}SN$: C, 75.77; H, 7.74; S, 10.77; N, 4.71. Found: C, 75.81; H, 7.84; S, 10.76; N, 4.61.

5-(4-Octylphenyl)-2,2′-bithienyl (**1b**), 5′-formyl-5-(4-octylphenyl)-2,2′-bithienyl (**2b**), and 5′-cyano-5-(4-octylphenyl)-2,2′-bithienyl (**CT2**) were synthesized in ways similar to those for **1a**, **2a** and **CT1**, respectively.

5-(4-Octylphenyl)-2,2′-bithienyl (1b). Mp 103 °C. ^{1}H NMR δ 0.91 (3H, t, J = 7.0 Hz, $-CH_3$), 1.23−1.42 (10H, m, $-(CH_2)_5CH_3$), 1.52−1.71 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.56 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_6CH_3$), 6.80 (1H, d, J = 3.5 Hz, Th-4-H), 6.90 (1H, d, J = 3.5 Hz, Th-3-H), 6.95 (1H, dd, J = 3.4 Hz, 1.0 Hz, Th-4′-H), 7.00 (1H, dd, J = 4.8 Hz, 1.0 Hz, Th-3′-H), 7.04 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.17 (1H, dd, J = 3.4 Hz, 4.8 Hz, Th-5′-H), 7.38 (2H, d, J = 8.4 Hz, Be-2-H, 6-H). Anal. Calcd for $C_{22}H_{26}S$: C, 74.58; H, 7.34; S, 18.08. Found: C, 74.41; H, 7.34; S, 18.14.

5′-Formyl-5-(4-octylphenyl)-2,2′-bithienyl (2b). Mp 140 °C. ^{1}H NMR δ 0.91 (3H, t, J = 7.0 Hz, $-CH_3$), 1.21−1.42 (10H, m, $-(CH_2)_5CH_3$), 1.52−1.73 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.57 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_6CH_3$), 6.90 (1H, d, J = 3.6 Hz, Th-4-H), 6.97 (1H, d, J = 3.6 Hz, Th-3-H), 7.10 (2H, d, J = 8.4, Be-3-H, 5-H), 7.20 (1H, d, J = 3.2 Hz, Th-3′-H), 7.41 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.71 (1H, d, J = 3.2 Hz, Th-4′-H), 9.66 (1H, s, −CHO). Anal. Calcd for $C_{23}H_{26}S_2O$: C, 72.25; H, 6.81; S, 16.75. Found: C, 72.16; H, 6.92; S, 16.80.

5′-Cyano-5-(4-octylphenyl)-2,2′-bithienyl (CT2). Mp 166 °C. ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.26−1.44 (10H, m, $-(CH_2)_5CH_3$), 1.50−1.72 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.58 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_6CH_3$), 6.88 (1H, d, J = 3.6 Hz,

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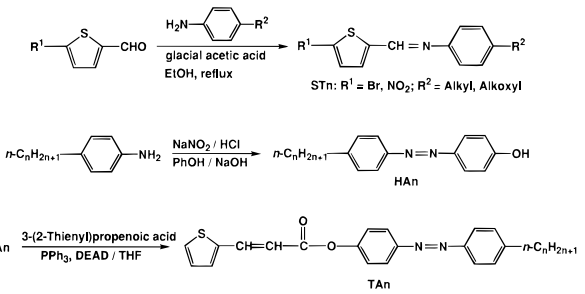
Scheme 2. Synthesis of STn and TAn



Th-4-H), 6.98 (1H, d, J = 3.6 Hz, Th-3-H), 7.10 (2H, d, J = 8.4 Hz, Be-3-H, H-5), 7.20 (1H, d, J = 3.3 Hz, Th-3′-H), 7.41 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.58 (1H, d, J = 3.3 Hz, Th-4′-H). IR (KBr, cm^{-1}) 2900, 2750, 2270, 1720, 1620, 1200, 1140, 970, 750. Anal. Calcd for $C_{23}H_{25}S_2N$: C, 72.82; H, 6.60; S, 16.89; N, 3.70. Found: C, 72.84; H, 6.61; S, 16.92; N, 3.71.

Preparation of STn. STn was synthesized following the route shown in Scheme 2.

2-[(4-Butylphenyl)iminomethyl]-5-nitrothiophene.[14] A mixture of 4-butylaniline (0.80 g, 500 mmol) and 5-formyl-2-nitrothiophene (0.82 g, 5.5 mmol) was heated to reflux in ethanol (30 mL) in the presence of a trace amount of glacial acetic acid for 18 h. The mixture was cooled to room temperature. Precipitated solid was filtered, washed with ethanol, and purified by column chromatography on alumina (ethyl acetate/hexane = 1/5 vol/vol). The title compound was obtained as pale-brown needles (1.03 g, 70% yield). ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.25−1.40 (2H, m, $-CH_2CH_3$), 1.52−1.66 (2H, m, $-CH_2CH_2CH_3$), 2.63 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_2CH_3$), 7.21 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.23 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.35 (1H, d, J = 4.0 Hz, Th-4-H), 7.91 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH═N). IR (KBr, cm^{-1}) 2980, 2900, 2380, 1530, 1500, 1330, 840, 730. Anal. Calcd for $C_{15}H_{16}SN_2O_2$: C, 62.50; H, 5.56; S, 11.11; N, 9.72. Found: C, 62.56; H, 5.54; S, 11.17; N, 9.81.

2-Nitro-5-[(4-pentylphenyl)iminomethyl]thiophene. This compound was similarly prepared in 71% yield from 4-pentylaniline and 5-formyl-2-nitrothiophene. ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.24−1.40 (4H, m, $-(CH_2)_2CH_3$), 1.53−1.67 (2H, m, $-CH_2(CH_2)_2CH_3$), 2.63 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_3CH_3$), 7.21 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.23 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.35 (1H, d, J = 4.0 Hz, Th−H-4), 7.92 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH═N). IR (KBr, cm^{-1}) 2960, 2900, 2370, 1520, 1500, 1330, 840, 730. Anal. Calcd for $C_{16}H_{18}SN_2O_2$: C, 63.58; H, 5.96; S, 10.60; N, 9.27. Found: C, 63.63; H, 5.93; S, 10.59; N, 9.26.

2-[(4-Hexylphenyl)iminomethyl]-5-nitrothiophene. This compound was prepared similarly in 71% yield from 4-hexylaniline and 5-formyl-2-nitrothiophene. ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.24−1.40 (6H, m, $-(CH_2)_3CH_3$), 1.53−1.67 (2H, m, $-CH_2(CH_2)_3CH_3$), 2.63 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_4CH_3$), 7.21 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.23 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.35 (1H, d, J = 4.0 Hz, Th-4-H), 7.92 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH═N). IR (KBr, cm^{-1}) 2970, 2900, 2380, 1530, 1500, 1330, 840, 730. Anal. Calcd for $C_{17}H_{20}SN_2O_2$: C, 64.56; H, 6.33; S, 10.13; N, 8.86. Found: C, 64.53; H, 6.36; S, 10.15; N, 8.85.

2-[(4-Heptylphenyl)iminomethyl]-5-nitrothiophene. This compound was similarly prepared in 73% yield from 4-heptylaniline and 5-formyl-2-nitrothiophene. ^{1}H NMR δ 0.90 (3H, t, J = 7.0 Hz, $-CH_3$), 1.24−1.40 (8H, m, $-(CH_2)_4CH_3$), 1.53−1.67 (2H, m, $-CH_2(CH_2)_4CH_3$), 2.63 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_4CH_3$), 7.21 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.23 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.35 (1H, d, J = 4.0 Hz, Th-4-H), 7.92 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH═N). IR (KBr, cm^{-1}) 2970, 2900, 2380, 1530, 1500, 1340, 830, 730. Anal. Calcd for $C_{18}H_{22}SN_2O_2$: C, 65.45; H, 6.67; S, 9.70; N, 8.48. Found: C, 65.46; H, 6.62; S, 9.76; N, 8.41.

2-Nitro-5-[(4-octylphenyl)iminomethyl]thiophene. This compound was similarly prepared in 76% yield from 4-octylaniline and 5-formyl-2-nitrothiophene. ^{1}H NMR δ 0.90 (3H,

(14) Nash, J. A.; Gray, G. W. *Mol. Cryst. Liq. Cryst.* **1974**, *25*, 199.

t, J = 7.0 Hz, $-CH_3$), 1.24−1.40 (10H, m, $-(CH_2)_5CH_3$), 1.53−1.67 (2H, m, $-CH_2(CH_2)_5CH_3$), 2.63 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_6CH_3$), 7.21 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.23 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.35 (1H, d, J = 4.0 Hz, Th-4-H), 7.92 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2970, 2900, 2370, 1530, 1500, 1340, 840, 730. Anal. Calcd for $C_{19}H_{24}SN_2O_2$: C, 66.28; H, 6.98; S, 9.30; N, 8.14. Found: C, 66.27; H, 7.00; S, 9.34; N, 8.20.

2-[(4-Butoxyphenyl)iminomethyl]-5-nitrothiophene. This compound was similarly prepared in 75% yield from 4-butoxyaniline and 5-formyl-2-nitrothiophene. ^{1}H NMR δ 0.98 (3H, t, J = 7.0 Hz, $-CH_3$), 1.40−1.60 (2H, m, $-CH_2CH_3$), 1.75−1.87 (2H, m, $-CH_2CH_2CH_3$), 4.00 (2H, t, J = 7.7 Hz, $-OCH_2(CH_2)_2CH_3$), 6.93 (2H, d, J = 8.8 Hz, Be-3-H, 5-H), 7.29 (2H, d, J = 8.8 Hz, Be-2-H, 6-H), 7.32 (1H, d, J = 4.0 Hz, Th-4-H), 7.91 (1H, d, J = 4.0 Hz, Th-3-H), 8.56 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2970, 2880, 2350, 1530, 1500, 1340, 840, 730. Anal. Calcd for $C_{15}H_{16}SN_2O_3$: C, 59.21; H, 5.26; S, 10.53; N, 9.20. Found: C, 59.13; H, 5.31; S, 10.58; N, 9.28.

2-Bromo-5-[(4-pentylphenyl)iminomethyl]thiophene. This compound was similarly prepared in 82% yield from 4-pentylaniline and 5-formyl-2-bromothiophene. ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz, $-CH_3$), 1.24−1.40 (4H, m, $-(CH_2)_2CH_3$), 1.53−1.67 (2H, m, $-CH_2(CH_2)_2CH_3$), 2.61 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_3CH_3$), 7.08 (1H, d, J = 3.9 Hz, Th-3-H), 7.12 (2H, d, J = 8.3 Hz, Be-3-H, 5-H), 7.17 (1H, d, J = 3.9 Hz, Th-4-H), 7.18 (2H, d, J = 8.3 Hz, Be-2-H, 6-H), 8.44 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2920, 2860, 1615, 1590, 1430, 970, 840, 800, 580. Anal. Calcd for $C_{16}H_{18}SNBr$: C, 57.14; H, 5.36; S, 9.52; N, 4.17; Br, 23.81. Found: C, 57.12; H, 5.31; S, 9.53; N, 4.18; Br, 23.85.

2-Bromo-5-[(4-hexylphenyl)iminomethyl]thiophene. This compound was similarly prepared in 82% yield from 4-hexylaniline and 5-formyl-2-bromothiophene. ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz, $-CH_3$), 1.23−1.40 (6H, m, $-(CH_2)_3CH_3$), 1.52−1.67 (2H, m, $-CH_2(CH_2)_3CH_3$), 2.61 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_4CH_3$), 7.08 (1H, d, J = 3.9 Hz, Th-3-H), 7.12 (2H, d, J = 8.3 Hz, Be-3-H, 5-H), 7.17 (1H, d, J = 3.9 Hz, Th-4-H), 7.18 (2H, d, J = 8.3 Hz, Be-2-H, 6-H), 8.44 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2920, 2860, 1615, 1590, 1430, 970, 840, 805, 570. Anal. Calcd for $C_{17}H_{20}SNBr$: C, 58.29; H, 5.71; S, 9.14; N, 4.00; Br, 22.86. Found: C, 58.31; H, 5.71; S, 9.13; N, 3.98; Br, 22.68.

2-Bromo-5-[(4-heptylphenyl)iminomethyl]thiophene. This compound was similarly prepared in 73% yield from 4-heptylaniline and 5-formyl-2-bromothiophene. ^{1}H NMR δ 0.88 (3H, t, J = 6.8 Hz, $-CH_3$), 1.22−1.41 (8H, m, $-(CH_2)_4CH_3$), 1.52−1.67 (2H, m, $-CH_2(CH_2)_4CH_3$), 2.61 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_5CH_3$), 7.08 (1H, d, J = 3.9 Hz, Th-3-H), 7.12 (2H, d, J = 8.3 Hz, Be-3-H, 5-H), 7.17 (1H, d, J = 3.9 Hz, Th-4-H), 7.18 (2H, d, J = 8.3 Hz, Be-2-H, 6-H), 8.44 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2920, 2860, 1620, 1590, 1430, 970, 840, 800, 570. Anal. Calcd for $C_{18}H_{22}SNBr$: C, 59.34; H, 6.04; S, 8.79; N, 3.85; Br, 21.98. Found: C, 59.35; H, 6.03; S, 8.75; N, 3.81; Br, 21.93.

2-Bromo-5-[(4-pentyloxyphenyl)iminomethyl]thiophene. This compound was similarly prepared in 75% yield from 4-pentyloxyaniline and 5-formyl-2-bromothiophene. ^{1}H NMR δ 0.94 (3H, t, J = 7.1 Hz, $-CH_3$), 1.37−1.51 (4H, m, $-(CH_2)_2CH_3$), 1.75−1.83 (2H, m, $-CH_2(CH_2)_2CH_3$), 3.96 (2H, t, J = 6.6 Hz, $-OCH_2(CH_2)_3CH_3$), 6.90 (2H, d, J = 7.6 Hz, Be-3-H, 5-H), 7.07 (1H, d, J = 3.9 Hz, Th-3-H), 7.15 (1H, d, J = 3.9 Hz, Th-4-H), 7.19 (2H, d, J = 7.6 Hz, Be-2-H, 6-H), 8.44 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2930, 2860, 1615, 1500, 1430, 1290, 1020, 840, 790, 580. Anal. Calcd for $C_{16}H_{18}SNOBr$: C, 54.55; H, 5.11; S, 9.09; N, 3.98; Br, 22.73. Found: C, 54.61; H, 5.14; S, 9.06; N, 3.91; Br, 22.74.

2-Bromo-5-[(4-hexyloxyphenyl)iminomethyl]thiophene. This compound was similarly prepared in 70% yield from 4-hexyloxyaniline and 5-formyl-2-bromothiophene. ^{1}H NMR δ 0.94 (3H, t, J = 7.1 Hz, $-CH_3$), 1.37−1.51 (6H, m, $-(CH_2)_3CH_3$), 1.75−1.82 (2H, m, $-CH_2(CH_2)_3CH_3$), 3.96 (2H, t, J = 6.6 Hz, $-OCH_2(CH_2)_4CH_3$), 6.90 (2H, d, J = 7.6 Hz, Be-3-H, 5-H), 7.07 (1H, d, J = 3.9 Hz, Th-3-H), 7.15 (1H, d, J = 3.9 Hz, Th-4-H), 7.19 (2H, d, J = 7.6 Hz, Be-2-H, 6-H), 8.44 (1H, s, −CH=N). IR (KBr, cm^{-1}) 2930, 2860, 1610, 1510, 1440, 1260, 1020, 840, 800, 570. Anal. Calcd for $C_{17}H_{20}SNOBr$: C, 55.73; H, 5.46; S, 8.74; N, 3.82; Br, 21.86. Found: C, 55.75; H, 5.41; S, 8.75; N, 3.81; Br, 21.93.

Preparation of TAn. TAn was synthesized following the route shown in Scheme 2.

4-Hexyl-4′-hydroxyazobenzene (HA6). 4-Hexylaniline (2.7 g, 15 mmol) was dissolved in HCl-water (5.4/27 mL/mL) mixture and diazotized by adding sodium nitrite (1.0 g, 15 mmol) dissolved in water (50 mL) at 0 °C. A solution of phenol (1.4 g, 15 mmol) and NaOH (1.8 g, 45 mmol) in water (40 mL) was added to the diazonium salt while stirring for 2 h at 0 °C. After filtration, **HA6** was isolated by column chromatography on silica gel (eluent, $CHCl_3$). Dark yellow solid was obtained as plates by recrystallization from hexane (2.1 g, 51% yield). Mp 91 °C. ^{1}H NMR δ 0.91 (3H, t, J = 6.8 Hz, $-CH_3$), 1.30−1.41 (6H, m, $-(CH_2)_3CH_3$), 1.61−1.70 (2H, m, $-CH_2(CH_2)_3CH_3$), 2.68 (2H, t, J = 7.6 Hz, $-CH_2CH_2(CH_2)_3CH_3$), 5.12 (1H, br s, −OH), 6.95 (2H, d, J = 8.8 Hz, 3-H, 5-H), 7.30 (2H, d, J = 8.3 Hz, 3′-H, 5′-H), 7.79 (2H, d, J = 8.3 Hz, 2′-H, 6′-H), 7.86 (2H, d, J = 8.8 Hz, 3-H, 5-H). IR (KBr, cm^{-1}) 3470, 1600, 1570, 1490, 1250, 860, 820. Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.60; H, 7.80; N, 9.93. Found: C, 76.55; H, 7.89; N, 10.02.

4-Butyl-4′-hydroxyazobenzene (HA4). The title compound was similarly synthesized in 43% yield. Mp 106 °C. ^{1}H NMR δ 0.94 (3H, t, J = 7.3 Hz, $-CH_3$), 1.30−1.41 (2H, m, $-CH_2CH_3$), 1.61−1.70 (2H, m, $-CH_2CH_2CH_3$), 2.68 (2H, t, J = 7.6 Hz, $-CH_2CH_2(CH_2)_2CH_3$), 5.28 (1H, br s, −OH), 6.94 (2H, d, J = 8.8 Hz, 3-H, 5-H), 7.30 (2H, d, J = 8.3 Hz, 3′-H, 5′-H), 7.79 (2H, d, J = 8.3 Hz, 2′-H, 6′-H), 7.86 (2H, d, J = 8.8 Hz, 3-H, 5-H). IR (KBr, cm^{-1}) 3480, 1600, 1580, 1500, 1250, 860, 820. Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.59; H, 7.09; N, 11.02. Found: C, 75.68; H, 7.11; N, 11.00.

4-Hydroxy-4-pentylazobenzene (HA5). The title compound was similarly synthesized in 41% yield. Mp 98 °C. ^{1}H NMR δ 0.91 (3H, t, J = 6.8 Hz, $-CH_3$), 1.30−1.41 (4H, m, $-(CH_2)_2CH_3$), 1.61−1.70 (2H, m, $-CH_2(CH_2)_2CH_3$), 2.68 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_3CH_3$), 5.28 (1H, br s, −OH), 6.95 (2H, d, J = 8.8 Hz, 3-H, 5-H), 7.30 (2H, d, J = 8.3 Hz, 3′-H, 5′-H), 7.79 (2H, d, J = 8.3 Hz, 2′-H, 6′-H), 7.86 (2H, d, J = 8.8 Hz, 3-H, 5-H). IR (KBr, cm^{-1}) 3480, 1600, 1570, 1500, 1240, 850, 820. Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.12; H, 7.46; N, 10.45. Found: C, 76.17; H, 7.40; N, 10.41.

4-Heptyl-4′-hydroxyazobenzene (HA7). The title compound was similarly synthesized in 53% yield. Mp 85 °C. ^{1}H NMR δ 0.88 (3H, t, J = 7.1 Hz, −CH3), 1.26−1.34 (8H, m, $-(CH_2)_4CH_3$), 1.61−1.70 (2H, m, $-CH_2(CH_2)_4CH_3$), 2.67 (2H, t, J = 7.6 Hz, $-CH_2(CH_2)_5CH_3$), 5.30 (1H, br s, −OH), 6.93 (2H, d, J = 8.8 Hz, 3-H, 5-H), 7.30 (2H, d, J = 8.3 Hz, 3′-H, 5′-H), 7.79 (2H, d, J = 8.3 Hz, 2′-H, 6′-H), 7.85 (2H, d, J = 8.8 Hz, 3-H, 5-H). IR (KBr, cm^{-1}) 3450, 1600, 1580, 1500, 1240, 850, 810. Anal. Calcd for $C_{19}H_{24}N_2O$: C, 77.02; H, 8.11; N, 9.46. Found: C, 77.08; H, 8.11; N, 9.41.

4-(4-Hexylphenyl)diazenylphenyl 3-(2-Thienyl)propenoate (TA6). 3-(2-Thienyl)propenoic acid (0.56 g, 3.2 mmol), **HA6** (0.91 g, 3.2 mmol), and diethyl azodicarboxylate (DEAD; 0.56 g, 3.2 mmol) were dissolved in dry THF (10 mL) at room temperature under dry argon atmosphere. Triphenylphosphine (0.91 g, 3.2 mmol) dissolved in dry THF (10 mL) was then added to the mixture with stirring at room temperature, and the mixture was stirred overnight. After the insoluble material was filtered off, the filtrate was concentrated under reduced pressure to give an orange solid. The residue was purified by column chromatography on silica gel (eluent, $CHCl_3$) to give **TA6** as orange powder (0.31 g, 23% yield). ^{1}H NMR δ 0.89 (3H, t, J = 7.1 Hz, $-CH_3$), 1.28−1.38 (6H, m, $-(CH_2)_3CH_3$), 1.61−1.71 (2H, m, $-CH_2(CH_2)_3CH_3$), 2.69 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_2CH_3$), 6.45 (1H, d, J = 15.8 Hz, Th−CH=C*H*−), 7.11 (1H, dd, J = 5.9 Hz, 1.1 Hz, Th-4-H), 7.31(2H, d, J = 8.8 Hz, Be-3′-H, 5′-H), 7.32 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.34 (1H, dd, J = 1.1 Hz, 3.6 Hz, Th-3-H), 7.47 (1H, dd, J = 3.6 Hz, 5.9 Hz, Th-5-H), 7.84 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.96 (2H, d, J = 8.8 Hz, Be-2′-H, 6′-H), 8.00 (1H, d, J = 15.8 Hz, Th−C*H*=CH−). IR (KBr, cm^{-1}) 3100, 2920, 1720, 1625, 1590, 1500, 1200, 1140, 960, 860, 720. Anal. Calcd for $C_{25}H_{26}SN_2O_2$: C, 71.78; H, 6.22; S, 7.66; N, 6.70. Found: C, 71.66; H, 6.32; S, 7.64; N, 6.68.

4-(4-Butylphenyl)diazenylphenyl 3-(2-Thienyl)propenoate (TA4). This compound was similarly prepared in

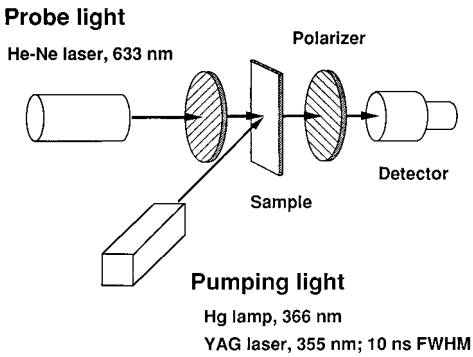


Figure 2. Schematic diagram for the measurement of photochemical N−I and I−N phase transition behavior in the transmission-mode analysis.

28% yield from 3-(2-thienyl)propenoic acid and **HA4**. ^{1}H NMR δ 0.89 (3H, t, J = 7.1 Hz, $-CH_3$), 1.29−1.38 (2H, m, $-CH_2$-CH_3), 1.61−1.71 (2H, m, $-CH_2CH_2CH_3$), 2.68 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_2CH_3$), 6.45 (1H, d, J = 15.8 Hz, Th−CH=C*H*−), 7.11 (1H, dd, J = 5.9 Hz, 1.1 Hz, Th-4-H), 7.31 (2H, d, J = 8.8 Hz, Be-3′-H, 5′-H), 7.32 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.34 (1H, dd, J = 1.1 Hz, 3.6 Hz, Th-3-H), 7.47 (1H, dd, J = 3.6 Hz, 5.9 Hz, Th-5-H), 7.84 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.96 (2H, d, J = 8.8 Hz, Be-2′-H, 6′-H), 8.00 (1H, d, J = 15.8 Hz, Th−C*H*=CH−). IR (KBr, cm^{-1}) 3150, 2950, 1720, 1625, 1595, 1500, 1205, 1140, 970, 860, 730. Anal. Calcd for $C_{23}H_{22}SN_2O_2$: C, 70.77; H, 5.64; S, 8.21; N, 7.18. Found: C, 70.73; H, 5.60; S, 8.14; N, 7.20.

4-(4-Pentylphenyl)diazenylphenyl 3-(2-Thienyl)propenoate (TA5). This compound was similarly prepared in 54% yield from 3-(2-thienyl)propenoic acid and **HA5**. ^{1}H NMR δ 0.88 (3H, t, J = 7.1 Hz, $-CH_3$), 1.29−1.38 (4H, m, $-(CH_2)_2$-CH_3), 1.60−1.71 (2H, m, $-CH_2(CH_2)_2CH_3$), 2.68 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_3CH_3$), 6.45 (1H, d, J = 15.8 Hz, Th−CH=C*H*−), 7.11 (1H, dd, J = 5.9 Hz, 1.1 Hz, Th-4-H), 7.31 (2H, d, J = 8.4 Hz, Be-3′-H, 5′-H), 7.32 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.34 (1H, dd, J = 1.1 Hz, 3.6 Hz, Th-3-H), 7.47 (1H, dd, J = 3.6 Hz, 5.9 Hz, Th-5-H), 7.84 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.96 (2H, d, J = 8.8 Hz, Be-2′-H, 6′-H), 8.00 (1H, d, J = 15.8 Hz, Th−C*H*=CH−). IR (KBr, cm^{-1}) 3150, 2900, 1720, 1625, 1595, 1500, 1200, 1140, 970, 860, 740. Anal. Calcd for $C_{24}H_{24}SN_2O_2$: C, 71.29; H, 5.94; S, 7.92; N, 6.93. Found: C, 71.31; H, 5.91; S, 7.98; N, 6.98.

4-(4-Heptylphenyl)diazenylphenyl 3-(2-Thienyl)propenoate (TA7). This compound was similarly prepared in 19% yield from 3-(2-thienyl)propenoic acid and **HA7**. ^{1}H NMR δ 0.89 (3H, t, J = 6.9 Hz, $-CH_3$), 1.27−1.38 (8H, m, $-(CH_2)_4$-CH_3), 1.61−1.72 (2H, m, $-CH_2(CH_2)_4CH_3$), 2.68 (2H, t, J = 7.7 Hz, $-CH_2(CH_2)_5CH_3$), 6.45 (1H, d, J = 15.8 Hz, Th−CH=C*H*−), 7.11 (1H, dd, J = 5.9 Hz, 1.1 Hz, Th-4-H), 7.31 (2H, d, J = 8.8 Hz, Be-3′-H, 5′-H), 7.32 (2H, d, J = 8.4 Hz, Be-3-H, 5-H), 7.34 (1H, dd, J = 1.1 Hz, 3.6 Hz, Th-3-H), 7.47 (1H, dd, J = 3.6 Hz, 5.9 Hz, Th-5-H), 7.84 (2H, d, J = 8.4 Hz, Be-2-H, 6-H), 7.96 (2H, d, J = 8.8 Hz, Be-2′-H, 6′-H), 8.00 (1H, d, J = 15.8 Hz, Th−C*H*=CH−). IR (KBr, cm^{-1}) 3100, 2930, 1720, 1625, 1595, 1490, 1200, 1140, 960, 870, 730. Anal. Calcd for $C_{26}H_{28}SN_2O_2$: C, 72.22; H, 6.48; S, 7.41; N, 6.48. Found: C, 72.35; H, 6.43; S, 7.38; N, 6.41.

Characterization. ^{1}H NMR spectra were recorded with a JEOL-400 (400 MHz) and a JEOL-500 (500 MHz) spectrometer in $CDCl_3$. Liquid-crystalline behavior, phase transition behavior, and melting points were measured on an Olympus Model BHSP polarizing microscope equipped with Mettler hot-stage Models FP-80 and FP-82. Thermotropic properties were determined with a differential scanning calorimeter (DSC; Seiko I&E SSC-5000) at a heating rate of 10 °C/min. Absorption spectra were measured on a Shimadzu UV-200 spectrometer.

Transmission-Mode Analysis of Photoresponse. Sample for examination of photochemical phase transition behavior was prepared by inserting LC into a 4-μm-gap cell. Figure 2 shows the experimental setup used for the observation of the photochemical phase transition behavior of LCs. The sample cell was thermostated and placed between two crossed polarizers and irradiated with monochromatic light at 366 nm which was isolated by the use of glass filters (Toshiba UV-35 and UV-D36A) from a 500-W high-pressure mercury lamp. A He−Ne laser (633 nm, 5 mW) was used as an analyzing light source and change in the light intensity transmitted through the cell was monitored with a photodiode, and the data were collected with a microcomputer.

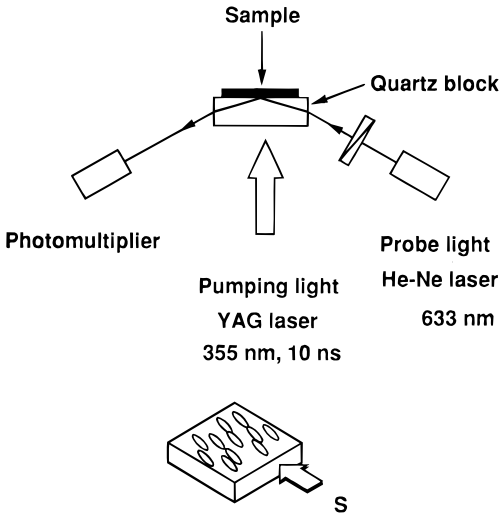


Figure 3. Experimental setup for reflection-mode analysis of photochemical N−I and I−N phase transition behavior.

In the time-resolved measurements, a Spectron SL805 Nd:YAG laser (the third harmonic, 355 nm; pulse width, 10 ns fwhm) was used as an excitation light source and transmittance of the He−Ne laser through crossed polarizers was measured with a Hamamatsu R-928 photomultiplier as a function of time and recorded with a storage scope (Iwatsu, DS-8631).

Reflection-Mode Analysis. Reflectivity, which is a fraction of light reflected at interface, alters as the change in refractive index of the sample, and the following expression can be obtained for incident light with *s*-polarization:[15]

$$R_s = \left(\frac{n_a \cos\theta_i - n_b \cos\theta_r}{n_a \cos\theta_i + n_b \cos\theta_r}\right)^2 \quad (1)$$

where R_s is reflectivity in *s*-polarization, n_a and n_b are refractive indexes of two materials, θ_i and θ_r are incident angle and refractive angle. In the reflection-mode analysis, we measured the intensity of the reflected light from the interface between the sample and the glass substrate to evaluate the change in the refractive index of the sample.

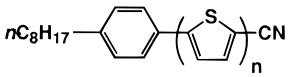
The sample was prepared on quartz block substrate that had been rubbed into one direction to align LC molecules. Figure 3 shows the schematic diagram for optical setup of the reflection-mode measurements. The sample was irradiated with a single pulse of the YAG laser at 355 nm, and the intensity of the probe light (He−Ne laser, at 633 nm) reflected at the interface between the sample and the glass substrate was measured with the photomultiplier as a function of time and recorded with the storage scope. The sample on the glass substrate was thermostated to show the N phase. The direction of alignment of LC molecules was parallel to the direction of incident probe light with *s*-polarization.

Results and Discussion

Liquid-Crystalline Behavior. Among the thiophene derivatives synthesized in this work, only **TAn** showed liquid-crystalline phase (nematic phase). Melting points of **CTn** and **STn** are listed in Tables 1 and 2, respectively. The phase transition temperatures of **TAn** are

(15) Born, M.; Wolf, E. *Principles of Optics*, 2nd ed.; Pergamon: Oxford, 1964; pp 38−51.

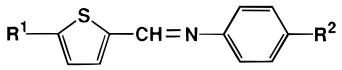
Table 1. Melting Point of CTn



CTn: n = 1, 2

n	mp (°C)
1	93
2	166

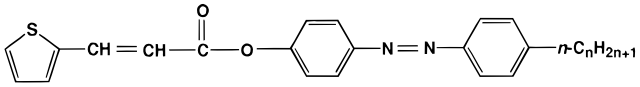
Table 2. Melting Points of STn



STn: R^1 = Br, NO_2; R^2 = Alkyl, Alkoxyl

R^1	R^2	mp (°C)
Br	C_5H_{11}	50
Br	C_6H_{13}	51
Br	C_7H_{15}	53
Br	OC_5H_{11}	86
Br	OC_6H_{13}	87
NO_2	C_4H_9	86
NO_2	C_5H_{11}	88
NO_2	C_6H_{13}	89
NO_2	C_7H_{15}	92
NO_2	C_8H_{17}	98
NO_2	OC_4H_9	79

Table 3. Phase Transition Temperatures of TAn[a]



TAn: n = 4, 5, 6, 7

n	phase transition temp (°C)
4	K 112 N 171 I (heating) K 74 N 169 I (cooling)
5	K 113 N 165 I (heating) K 81 N 161 I (cooling)
6	K 114 N 157 I (heating) K 68 N 156 I (cooling)
7	K 110 N 134 I (heating) K 81 N 129 I (cooling)

[a] K, crystal; N, nematic; I, isotropic.

also shown in Table 3. It is well-known that many compounds that have a structure similar to **CTn** and **STn** but phenyl moieties in place of thienyl moieties show liquid-crystalline phases. This fact indicates that incorporation of the thiophene ring into a central part of the core is unfavorable to show the liquid-crystalline phase because of the bent structure of the 2,5-thienylene derivatives. On the other hand, **TAn** with the thiophene unit at the end of the molecule showed the N phase. It is interesting to note that in **TAn** the crystal to N phase transition temperature (T_{KN}) is not affected significantly as the number of carbon atom in the flexible spacer (n) increases, but N−I phase transition temperature (T_{NI}) decreases as n increases. Furthermore, **TAn** showed quite a wide temperature range for the N phase on cooling. The values of T_{KN} observed on cooling were lower by 30−40 °C than those observed on heating. We chose **TA6** for examination of the photoresponsive behavior in the following experiments since it showed the N phase in the lowest temperature range among **TAn** (n = 4, 5, 6, and 7).

Photoisomerization Behavior. Figure 4 shows the absorption spectra of **TA6** in $CHCl_3$ (2.3×10^{-5} M) at room temperature (26 °C). Two absorption maxima

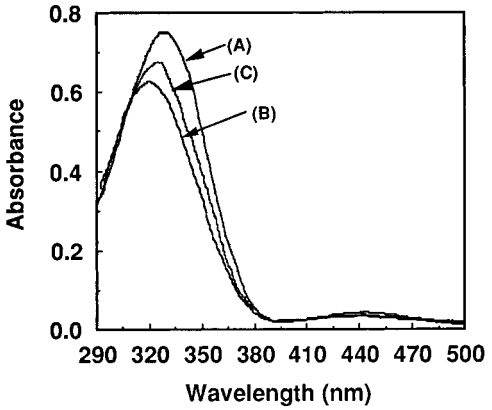


Figure 4. Absorption spectra of **TA6** in chloroform. (A) before irradiation; (B) after irradiation at 366 nm; (C) after irradiation at >450 nm. [**TA6**] = 2.3×10^{-5} M.

were observed at 330 and 450 nm: the former is due to $\pi-\pi^*$ transition and the latter is due to n−π^* transition of the azobenzene moiety. In **TA6** there are two chromophores which absorb light at 300−500 nm: the azobenzene unit and thienylpropenoate moiety. The absorption spectra of **TA6** indicate that the absorption in this wavelength is mainly due to the azobenzene moiety. Photoirradiation of **TA6** at 366 nm caused decrease of the absorption maximum at 330 nm owing to trans−cis photoisomerization of the azobenzene moiety in **TA6** (Figure 4B). After irradiation at >450 nm, the absorbance at 330 nm gradually increased, which indicates that photoisomerization of **TA6** took place reversibly in solution as in ordinary azobenzene derivatives without the thiophene moiety.

Photochemical Phase Transition Behavior. Figure 5 shows that photoirradiation of the 4-μm-gap cell containing **TA6** at 366 nm resulted in N−I phase transition of **TA6** as probed by loss of birefringence, and when photoirradiation was ceased and the irradiated sample was kept in the dark at the same temperature, I−N phase transition took place both at 155 °C (Figure 5A) and at 70 °C (Figure 5B). This behavior can be interpreted in terms of trans−cis photoisomerization of the azobenzene moiety, leading to the N−I phase transition, and thermal cis−trans back isomerization of the azobenzene moiety in the dark, leading to the I−N phase transition, as observed in other azobenzene LCs.[3] The photochemical N−I and the thermal I−N phase transition could be induced repeatedly.

In Figure 6, the time required for the thermal I−N phase transition is plotted as a function of temperature. At each temperature, the 4-μm-gap cell containing **TA6** was irradiated at 366 nm until the sample lost birefringence completely and the irradiated sample was kept at the same temperature in the dark. The time for the thermal I−N phase transition was defined as the time required to raise the transmittance from 0% to 90% of the maximum value. It is clear that the time for the I−N phase transition decreased as the temperature increased, typically 30 s at 70 °C to 10 s at 155 °C. This is mainly due to faster cis−trans thermal isomerization of the azobenzene moiety in **TA6** at higher temperature. It is worth mentioning here that a wide temperature range (70−155 °C) was available for measurements of the I−N phase transition behavior since **TA6** showed supercooled N phase to such low temperature as 70 °C on cooling, while it exhibited T_{KN} of 114 °C on heating.

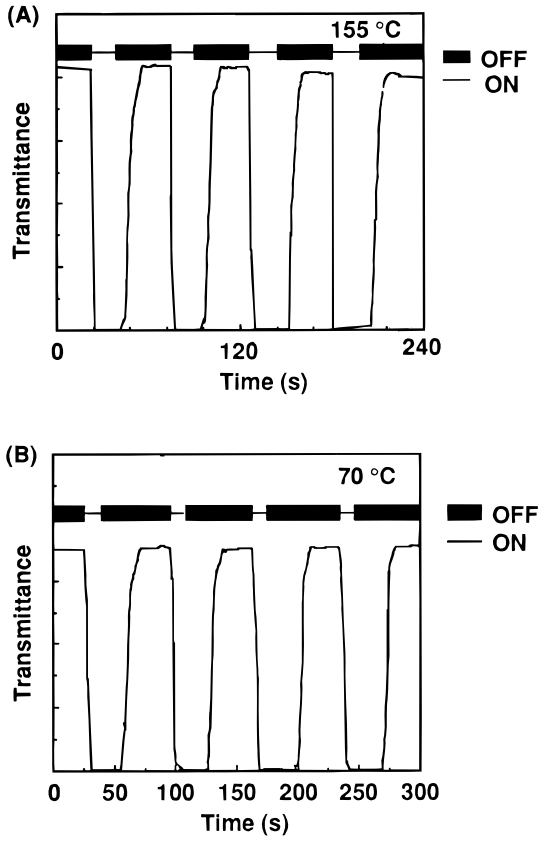


Figure 5. Photochemical N−I phase transition and thermal I−N transition of **TA6**. Transmittance through crossed polarizers was measured as a function of time. Photoirradiation was performed at 366 nm: (A), at 155 °C; (B), 70 °C.

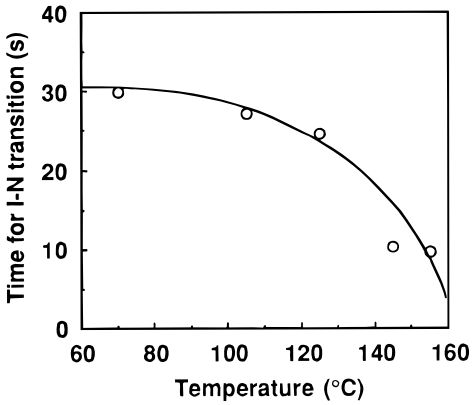


Figure 6. Time required for I−N thermal phase transition of **TA6** as a function of temperature.

Figure 7 shows the results of the time-resolved measurements on the photochemical N−I phase transition of **TA6** where the change in transmittance of the He−Ne laser through crossed polarizers, with the 4-μm-gap cell containing **TA6** between them, is indicated as a function of time after irradiation of a single pulse of the laser. At 155 °C (Figure 7A) and 70 °C (Figure 7B), the response time for the N−I phase transition, which was defined as the time necessary to reduce the transmittance to 10% of the maximum value, was nearly the same (8 ms). When the laser power was increased (4.5 mJ/cm^2 → 8.0 mJ/cm^2), the response time for the N−I phase transition became short as shown in Figure 8. This phenomenon results from increase of the cis isomers of **TA6** formed by pulse irradiation with higher intensity.

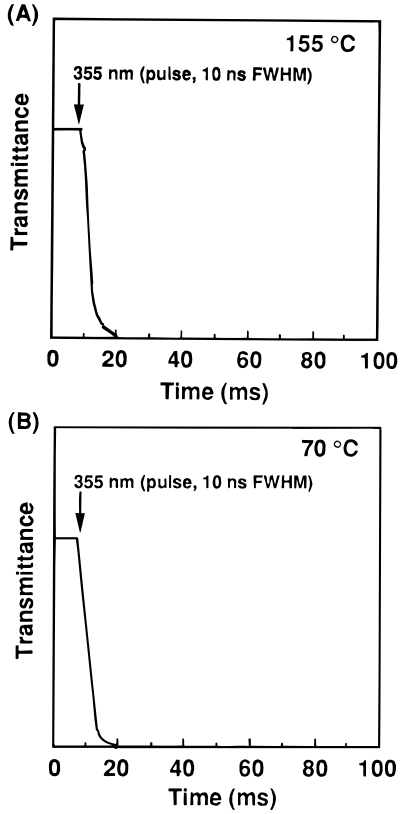


Figure 7. Time-resolved measurements of the photochemical N−I phase transition induced by pulse irradiation in **TA6** evaluated by the transmission-mode analysis. (A) 155 °C; (B) 70 °C. Laser power, 4.5 mJ/cm^2.

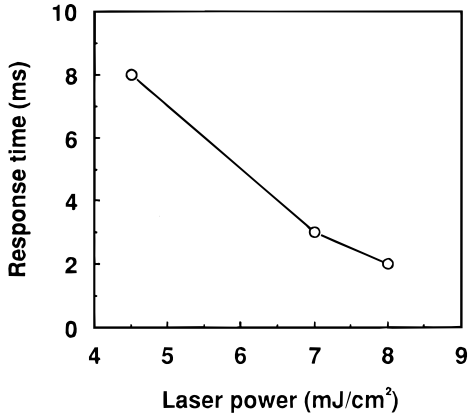


Figure 8. Response time of the photochemical N−I phase transition of **TA6** as a function of laser power at 155 °C evaluated by the transmission-mode analysis.

Transient absorption spectroscopy has shown that the trans−cis photoisomerization of azobenzene derivatives occurred within 10 ns.[3b] Therefore, it was expected that the photochemical N−I phase transition of **TA6** would be completed within 10 ns. However, the response times observed were several milliseconds as demonstrated in Figure 8, which results from the large extinction coefficient of **TA6** at 355 nm ($\epsilon > 10^4$ in Figure 4). In other words, photons are absorbed only at the surface of **TA6** and the trans−cis photoisomerization takes place at the surface, and cis isomers thus formed diffuse through the 4-μm-gap cell. The response time of several milliseconds is, therefore, the sum of those of at least two processes: photoisomerization and diffusion of the cis forms. It is expected that the diffusion process had temperature dependence, and the

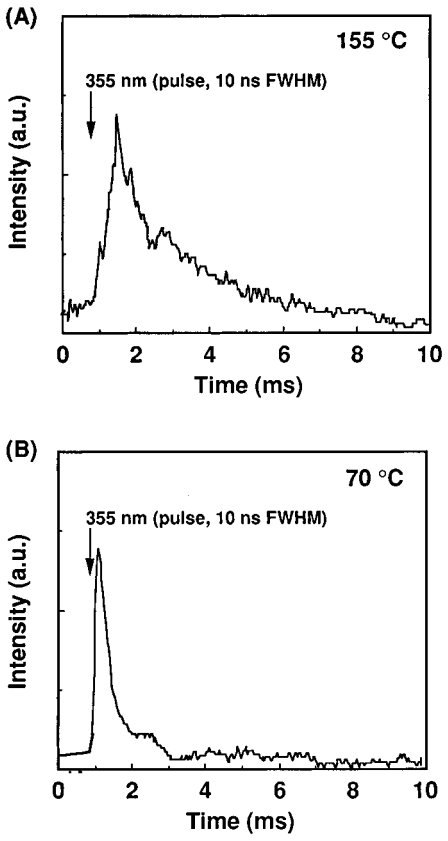


Figure 9. Time-resolved measurements of the photochemical N−I phase transition of **TA6** evaluated by the reflection-mode analysis. (A) at 155 °C; (B) at 70 °C.

response time at 155 °C was shorter than that at 70 °C. However, the experimental result was not the case. This is probably due to the small change in the diffusion coefficient at these two temperatures in such an anisotropic medium as NLCs.

Photochemical Phase Transition Behavior Evaluated by Reflection-Mode Analysis.[16] Figure 9 shows the results of the time-resolved measurements obtained in the reflection-mode analysis where **TA6** molecules were aligned in a homogeneous manner with the molecular long axis oriented parallel to the probe light (*s*-polarization) as shown in Figure 3. The intensity of the probe light reflected at the interface increased in 100 μs at 70 °C and in 400 μs at 155 °C on pulse irradiation at 355 nm and decayed in 1 ms at 70 °C and in 4 ms at 155 °C, respectively.

The refractive index of LCs shows anisotropy: the refractive index of light polarized parallel to the direction of molecular long axis of LCs (n_e) is much larger than that of light polarized perpendicular to the direction of the molecular long axis of LCs (n_o) when the LC molecules are uniaxially aligned. This is true for the azobenzene LCs with trans form of the azobenzene moieties. However, the refractive index of the azobenzene LCs (n) is very similar when they are in the I phase irrespective of trans and cis forms of the azobenzene moieties, and the following relation can in general be obtained: $n_o < n < n_e$. When the probe light with *s*-polarization is incident upon the interface where the LC molecules are aligned parallel to the direction of the incident light, the refractive index of the LC molecules is n_o. If the N−I phase transition is induced by trans−cis photoisomerization of the azobenzene LC, the refractive index is increased from n_o to n. Under the present experimental setup, the refractive index of the sample (**TA6**) is always larger than that of the glass substrate, and an increase in reflectivity means an increase in the refractive index of the sample as evidenced by eq 1. Thus, the results shown in Figure 9 may be interpreted in terms of the change in the refractive index of **TA6** molecules from n_o to n as a result of the N−I phase transition induced on pulse irradiation, followed by recovery of the initial N state at the surface of the glass substrate. It is worth noting here that in the reflection-mode measurements the change in reflectivity of the probe light is very fast: in the transmission-mode analysis, the change in transmittance associated with the N−I phase transition was observed in several milliseconds (Figure 7) and the recovery of the initial N phase took several tens seconds due to thermal cis−trans back-isomerization of the azobenzene moieties. On the other hand, in the reflection-mode analysis the change in reflectivity associated with the N−I phase transition was observed in 100 μs at 70 °C and in 400 μs at 155 °C, and the recovery of the N was completed in 1 ms at 70 °C and in 4 ms at 155 °C, respectively. These results indicate that the recovery mechanism in the reflection-mode analysis differs from that in the transmission-mode analysis in which the recovery process mainly depends on the cis−trans back-isomerization of the azobenzene moiety. The molar extinction coefficient of the azobenzene moiety is very large at 355 nm ($\epsilon > 10^4$), and hence pumping light is absorbed entirely at the surface of the sample. Then, the trans−cis photoisomerization is also induced near the surface. Consequently, the N−I phase transition occurred only in the surface, leaving the bulk area intact as an N phase. In the reflection-mode analysis, the probe light can penetrate only in the surface area, so if molecules in the cis form produced at the surface by photoirradiation diffuse into the bulk phase and molecules in the trans form in the bulk phase replace them, recovery of the initial N phase can be achieved without the slow cis−trans back-isomerization process. Since the diffusion and reorientation process is much faster than the cis−trans back-isomerization process, optical switching has become much faster in the reflection-mode analysis.

Faster response of **TA6** at 70 °C than at 155 °C may result from higher orientation of the LC molecules at lower temperature. At 155 °C which is close to T_{NI}, the phase structure is already disorganized to some extent and the order parameter of the LC is low.[16] The change in the refractive index, therefore, is very small before and after pulse irradiation. On pulse irradiation the N−I phase transition is induced completely at high temperatures. However, at lower temperatures, the LC molecules are highly oriented and the order parameter is also high. Under such circumstances, the N−I phase transition is assumed to be induced locally, and this partial phase transition makes the change in the reflectivity faster at 70 °C than at 155 °C. The phase is well organized at 70 °C and has high tendency to restore the phase structure on application of perturbation. As a result, at 70 °C the reflectivity returned to the initial state faster than at 155 °C, although the diffusion is evidently effective at higher temperature.

(16) Shishido, A.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Tamai, N. *J. Phys. Chem. B* **1997**, *101*, 2806.

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