Characterization of 9-(*p*-Substituted Benzylidenehydrazono)fluorenes

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(Received July 17, 1996)

The title azine was obtained by a reaction of the corresponding fluorenone hydrazone and *p*-substituted benzaldehyde. The hydrazone formed from the unsymmetrical fluorenone afforded configurational isomers; the *E*-isomer was thermodynamically more stable than the *Z*-isomer. The structure of the title azines, derived from symmetrical fluorenone, was assigned to be (*s-trans*/*E*) form. The azines from unsymmetrical fluorenone gave isomeric mixtures due to the 9-iminofluorene moiety. The electronic spectra of these azines show an intramolecular charge transfer; the red shift beyond 250 nm is observed in the case of 9-[*p*-(diethylamino)benzylidenehydrazono]-2,4,7-trinitrofluorene, compared to the mother azine. 9-[*p*-(Pentyloxy)benzylidenehydrazono]-2,7-dinitrofluorene and some of the homologs possess a liquid-crystalline property; the phase-transition temperature of the dinitro compound is K (172 °C) M_1 (185) M_2 (187) I between the crystalline and liquid phases.

A clarification of the chemical and physical properties of the title azines was made as a part of our continuous studies on the synthesis and characterization of polycyclic aromatic hydrocarbons.1) 9-(Benzylidenehydrazono)fluorene2) (**1**, R=R′=H, Chart 1) is already known, but is scarcely mentioned concerning its properties. In general, the reaction of azine substrates, or 2,3-diaza-1,3-butadiene derivatives, has been widely studied as a moiety of heterocyclic compounds.3) Following the many applications of azine in synthesis, studies concerning the stereochemistry and electronic structure of the 2,3-diaza-1,3-butadiene moiety have been increasing recently.4—6) Furthermore, these stereochemical and electronic properties of azine result in new applications of these compounds on, for example, liquid-crystal fields.7)

Based on this background, **1** is discussed in this paper concerning the following three points. The first is related to the stereochemistry of **1**, regarding to a N–N conformation and two C=N configurations. The configuration of fluorenone hydrazone (**2**), precursor of **1**, is also mentioned. The second is to clarify the contribution of the resonance interaction through a central N–N bond in the unsymmetrical azines. An intramolecular charge transfer is expected by substitutions of both the electron-withdrawing group (nitro) at the fluorene moiety and the electron-donating group (alkoxy or dialkylamino) at the benzylidene part. The third is the application of **1** having a long alkyloxy chain at the *p*-position of the benzylidene. The azine **1** is presumably a planar and wide molecule, and the stacking of **1** is expected to be a rod-type liquid crystal.

This paper deals with a stereochemical consideration of **1** based on the NMR data, the electronic effect of **1** based on the electronic spectra, and its possibility as a liquid crystal from the DSC curves, respectively.

Results and Discussion

Structure of Fluorenone Hydrazones (2). The reaction of fluorenone with hydrazine hydrate in ethanol or in acetic acid afforded the corresponding hydrazone, as has been reported (Chart 1). Although fluorenone hydrazone (**2a**, Chart 2),2) 2-nitro- (**2b**),8) 2,7-dinitro- (**2c**),9) and 2,4,7-trinitrofluorenone hydrazone (**2e**)10) are already known, they have lacked a NMR assignment.

The ^{1}H NMR spectrum of **2a** shows signals at $\delta = 7.90$, 7.73, and 6.41 corresponding to the H(8), H(1), and amino protons, respectively. About 5% of NOE is observed between the peaks of H(8) and the amino signal. This result indicates that the peak of H(1) appears at a higher field than that of H(8), which is situated opposite to the lone pair of the Schiff's base nitrogen; this is consistent with the reported direction.11,12) This phenomenon is explained based on the paramagnetic shift of H(8) due to an interaction between H(8) and the amino nitrogen (or, intramolecular hydrogen bond), but not the diamagnetic shift of H(1) due to the influence of the C=N nitrogen.12) Although the distance between H(8) and the lone pair of amino nitrogen is estimated to be less than 0.20 nm, the distance between H(1) and the lone pair of C=N nitrogen is 0.25 nm, based on the molecular model.

Although configurational isomers were confirmed in the cases of **2b** and **2e**, it is difficult to separate them into each of the isomers. The ^{1}H chemical shifts of **2b** were assigned based on the 2D NMR; a part of them is shown in Chart 3. NOE (5—6%) was observed between the peaks at $\delta = 7.94$—7.98 and at 6.71 in the case of (*E*)-**2b**, and between those at $\delta = 8.77$ and 6.70 in the series of (*Z*)-**2b**. The electron-withdrawing nitro group in both (*E*)- and (*Z*)-**2b** influences to the amino protons, which appear more downfield ($\Delta\delta =$ ca. 0.3 ppm) than those of **2a**.

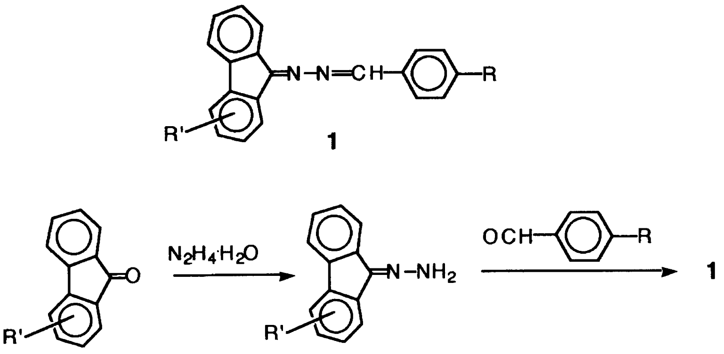
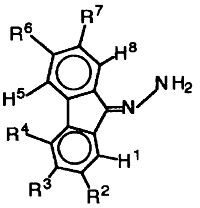
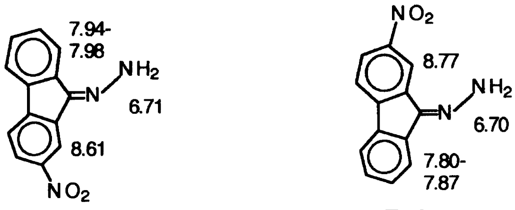


Chart 1.



2a ($R^2 = R^3 = R^4 = R^6 = R^7 = H$)
2b ($R^2 = NO_2$, $R^3 = R^4 = R^6 = R^7 = H$)
2c ($R^2 = R^7 = NO_2$, $R^3 = R^4 = R^6 = H$)
2d ($R^3 = R^6 = NO_2$, $R^2 = R^4 = R^7 = H$)
2e ($R^2 = R^4 = R^7 = NO_2$, $R^3 = R^6 = H$)

Chart 2.



***E*-2b** ***Z*-2b**

Chart 3. ^{1}H chemical shifts of isomeric **2b**.

Table 1 shows the formation ratio of the (*E*) and (*Z*) isomers in the synthesis of **2b** by the reaction of 2-nitrofluorenone with hydrazine hydrate (3 molar amounts to the ketone) in a solvent. The ratio was determined by a comparison of the peaks on ^{1}H NMR. Only the Wolff–Kishner reduction occurred, giving 95% of 2-nitrofluorene, when hexanol was used as a solvent (at 158 °C).

Isomeric mixtures of **2b** were obtained over an 80 % yield in all cases of Table 1. The ratio of the (*E*) isomer increased by an elongated reaction time, by an elevated reaction temperature, or by the addition of acid. It appears that the (*E*) isomer is thermodynamically more stable than the (*Z*) isomer, similar to the other cases.[12)]

Stereochemistry of 9-(*p*-Substituted Benzylidenehydrazono)fluorenes. The title azines were obtained by the reaction of **2** with *p*-substituted benzaldehydes (Chart 1). Each of azines derived from symmetrical **2a**, **2c**, and **2d** was a simple compound, based on their NMR spectra; however, the azines obtained from unsymmetrical **2b** and **2e** were isomeric mixtures.

Table 1. Formation Ratio of *E*- and *Z*-**2b**

Solvent	React. Temp °C	Time h	*E*/*Z*
EtOH	78	6	57:43
EtOH	78	24	63:37
EtOH[a)]	78	6	85:15
BuOH	118	6	78:22

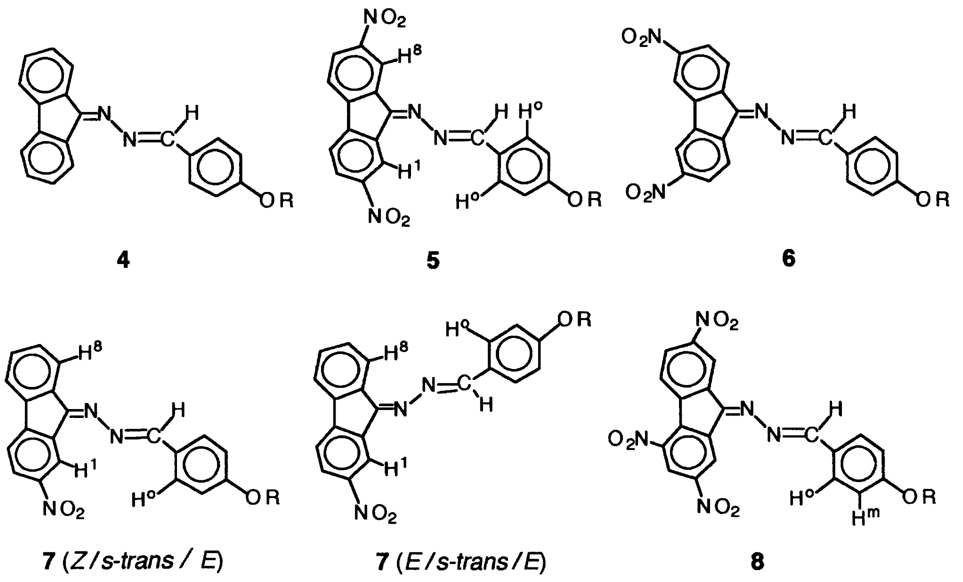
a) Trifluoroacetic acid (equiv mol to the ketone) was added.

Many of the symmetrical aldazines formed from benzaldehydes have been assigned to have the (*EE*) configuration among three possibilities ((*EE*), (*EZ*), and (*ZZ*)).[11,13—15)] Some of the symmetrical ketazines derived from the acetophenone derivatives were obtained as the (*EZ*) form, in addition to the stable (*EE*) form.[11,13,16)] The conformation of the N–N bond in these azines is *s-trans* or *gauche*.[5,6,15)] *p*-Hexyloxybenzaldehyde azine (**3**)[17)] was shown to be single in solution by ^{1}H NMR, and should be assigned to the (*EE*) form.

The configuration of the *p*-alkoxybenzylideneimine moiety of 9-[*p*-(alkoxy)benzylidenehydrazono]fluorene (**4**, Chart 4) is considered to be the (*E*) form, which is more stable than the (*Z*) isomer by about 2.8 kcal mol^{-1}, based on a consideration of the molecular models. The torsional conformations around the N–N bond of **4**, other than (*s-trans*), are less stable than (*s-trans*), because of the bulky, planar fluorenylidene moiety, compared to the ketazine derived from the nonplanar acetophenone.

Therefore, the stereochemistry of the isolated azines, **4**, 2,7-dinitro- (**5**), and 3,6-dinitro derivative (**6**) is predicted to be (*s-trans/E*). The ^{1}H NMR signals of the H(1), H(8), and H(*o*) of **5** ($R = C_6H_{13}$) appear at $\delta = 9.70$, 8.86, and 7.99, respectively. About 11 and 17% of NOE are observed between H(1) and H(*o*), and between H(*o*) and the benzylic proton, respectively. These values are considered to be reasonable for a planar molecule **5**, because the distances between H(1) and H(*o*), and between H(*o*) and the benzylic proton, are estimated to be about 0.26 and 0.25 nm, respectively. Compared to H(8) ($\delta = 8.86$) of **5**, the H(1) ($\delta = 9.70$) shifts downfield because of the influence of the close benzylideneamino nitrogen.

The isomerism of azines **7** and **8**, derived from **2b** and **2e**, respectively, should be due to the configuration of the fluorenylideneamine moiety, as shown in Chart 4. The assignment of **7** (*Z/s-trans/E*) ($R = C_6H_{13}$) is based on the NOE (11%) between H(1) ($\delta = 9.58$) and H(*o*). NOE (9%) was detected between H(8) ($\delta = 8.65$) and H(*o*) in the case of **7** (*E/s-trans/E*) ($R = C_6H_{13}$).



4 **5** **6**

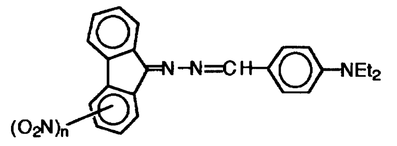
7 (*Z*/*s-trans*/*E*) **7** (*E*/*s-trans*/*E*) **8**

Chart 4.

An isomeric mixture of (*E/s-trans/E*) and (*Z/s-trans/E*) of **7** having a similar ratio (44/56) was obtained by heating (150 °C, 1h) pure **7** (*Z/s-trans/E*) ($R=C_6H_{13}$), pure **7**(*E/s-trans/E*) ($R=C_6H_{13}$), or their mixture, respectively. The (*Z/s-trans/E*) form is explained to be a slightly more stable than the (*E/s-trans/E*) form, because the ratio did not significantly changed at elevated temperature (180 °C). The reason can not be clearly explained at present. A possible explanation is that the acidity of H(1) of **7** is stronger than H(8) due to the ortho nitro group. Therefore, a stronger hydrogen bond between H(1) and the benzylideneamino nitrogen in (*Z/s-trans/E*) form than the interaction between H(8) and the benzylideneamino nitrogen in (*E/s-trans/E*) form causes a higher stability of the (*Z/s-trans/E*) form.

Electronic Spectra of 9-(*p*-Substituted Benzylidenehydrazono)fluorenes. By comparing the ^{1}H NMR data of **4**, **5**, **6**, **7**, and **8**, the substitution of nitro group(s) to the fluorenylidene moiety influences the benzylidene part through an azine bond. Proton signals at the benzylic, H(*o*), and H(*m*) of **8** ($R=C_6H_{13}$) appear more downfield ($\Delta\delta=0.25$, 0.12, and 0.09 ppm, respectively) compared to those of **4** ($R=C_6H_{13}$). Also, a paramagnetic effect ($\Delta\delta=0.06$) is observed at the oxymethylene protons of the *p*-alkyloxy group.

The electronic spectra of these azines were compared with those of *p*-diethylamino-substituted azines, **9a**, **9b**, and **9c** (Chart 5). The wavelengths of the maximal absorption are not so clear because of their broad bands. The longest wavelength of the band is difficult to compare with each other, due to the low solubilities of the azines. Table 2 gives the wavelength at log $\varepsilon=4.00$ of the absorption band of the azines in dichloromethane and acetonitrile. This comparison is considered to make it easy to evaluate the electronic properties of these azines.



9a; 2-nitro-
9b; 2,7-dinitro-
9c; 2,4,7-trinitro-

Chart 5.

Table 2. Electronic Spectra of Azines

Compound	Wavelength[a)]/nm	
	CH_2Cl_2	CH_3CN
1 ($R=R'=H$)	369	364
4 ($R=C_6H_{13}$)	402	401
7[b)] ($R=C_6H_{13}$)	422	417
5 ($R=C_6H_{13}$)	436	429
6 ($R=C_6H_{13}$)	463	451
8[b)] ($R=C_6H_{13}$)	476	463
1 ($R=NMe_2$, $R'=H$)	490	490
9a[b)]	527	526
9b	575	566
9c[b)]	630	617

a) Wavelength at log $\varepsilon=4.00$. b) *E*/*Z* isomeric mixture.

The spectrum of **7** (*E/s-trans/E*) ($R=C_6H_{13}$) is very similar to that of (*Z*) isomer. A red shift of the absorption was observed upon increasing the number of nitro groups, or by substitution at the 3,6-positions corresponding to para to the azine bond instead of the 2,7-positions of the fluorene moiety. A red shift also occurs by the substitution of a diethylamino group that is more electron-donating than the alkoxy group in the benzylidene part. The red shift of **9c**, compared to **1** ($R=R'=H$), is beyond 260 nm in dichloromethane. This shift is due to the intramolecular charge transfer from the findings that the shift is larger in a nonpolar solvent than in a polar solvent.

Properties of Substituted 9-(Benzylidenehydrazono)fluorenes as Liquid Crystals. These azines are planar and wide molecules, and lack axes of symmetry; it seems that these azines are not discotic liquid crystals. The molecular area of 9-[*p*-(hexyloxy)benzylidenehydrazono]fluorene-4-carboxylate (**1**, $R=H$, $R'=4\text{-COO}^-$) was estimated to be 0.51 nm^2/molecule by means of a measurement of the π–A isotherm of a monolayer prepared on water using the corresponding cadmium salt.[18] This value is about twice the molecular area of *p*-substituted benzoate (0.26 nm^2/molecule). It is clear that the azinecarboxylic acid is possibly stacked as firm as *p*-substituted benzoate. This finding assumes that the liquid crystal from the title azines is presumably rod-type, but not discotic.

The phase-transition temperature of the azines was measured during the heating process, as is shown in Table 3. Azine **4**, having no nitro group, shows only a sharp melting point in all cases of various number of carbon atoms of the alkoxy group (n = 1—16). Also, **8** (n = 6, 8, 12, 16) has a melting point of narrow range, in spite of it being a configurational isomeric mixture. The broad transition interval of **7** (Table 3) is observed as a mixed liquid crystal of configurational isomers (E/Z = 44/56). Each pure **7** (*E/s-trans/E*) (R = C_6H_{13}; mp 130.5—133.0 °C) and its isomer (*Z/s-trans/E*) (R = C_6H_{13}; mp 130.0— 132.5 °C) show no liquid-crystalline property by observations using a polarized microscope.

The nitro groups in **5** and **6** act in two ways to the properties of azines as rod-type liquid crystals.[19] One is action as the terminal group of a molecule, in which the nitro group increases the polarity of the molecule and pushes up the mesophase temperature. The other influences as the side-chain group of the molecule, which spreads the molecular width, and increases the mobility between the molecules; it pulls down the transparent point of a liquid crystal. In the case of **6**, the nitro group resonates effectively through the azine bond with the benzylidene part, thus increasing the polarity of the molecule. On the other hand, the nitro group of **5** does not increase the polarity, and situates in the lateral direction of the molecule, compared to that of **6**. A combination of these two factors results in the different properties of **5** and **6**.

DSC curves of **5** (R = C_5H_{11}, C_6H_{13}) show three endothermic peaks during the heating process, as is shown in Table 3. The heat of endotherms is also shown. Although the presence of different mesophases was confirmed by an examination using a polarized microscope, the type of mesophases could not identified at present. The thermal behavior seems not to be reversible, because only two exothermic peaks can be recognized during the cooling process; for example, these are at 181 °C (ΔH = 0.3 KJ mol^{-1}) and 161 °C (ΔH = 31 KJ mol^{-1}) in the case of **5** (R = C_6H_{13}). Azines **5** and **6** are unique examples of rod-type liquid crystal having an unfamiliar molecular shape.

Table 3. Phase-Transition Temperature of Azines

Compd	No. of R[a]	Phase-transition temp[b]/°C		
		K	M	I
7[c]	6	104		114
	7	109		115
5	4	188		197
	5	172	(185)[d]	187
		[26][e]	[0.3][e]	[0.3][e]
	6	171	(176)[d]	182
		[30][e]	[1.4][e]	[0.3][e]
6	7	215		224
	8	220		224
	9	232		235

a) Carbon number of alkoxy group. b) K: crystal; M: mesophase; I: liquid. c) *E/Z* isomeric mixture. d) Second phase-transition temperature. e) Enthalpy change during heating process (KJ mol^{-1}).

Experimental

The melting points are uncorrected. The NMR spectra (0.7 ml $CDCl_3$) were recorded with a Varian VXR-300. The DSC curves and electronic spectra were obtained with a Rigaku DSC-8230 and a Shimadzu UV-180. The mass spectra and elemental analyses were measured with a JMS-AX 500 (JEOL) and with an EA 1108 CHNS-O (Fison Instruments).

Fluorenone Hydrazone (2a). A solution of fluorenone (0.90 g, 5.0 mmol) in EtOH (40 ml) was refluxed for 6 h with hydrazine hydrate (80%, 1.0 ml, 16.5 mmol). Upon cooling, the deposit was collected by filtration, washed with water, and recrystallized from EtOH to give 0.95 g (88%) of **2a**: Mp 152.5—154.5 °C (lit,[2] mp 149 °C); ^{1}H NMR δ = 6.41 (2H, NH_2), 7.30 (1H, td, J = 7.1, 0.9 Hz, H_2), 7.32 (1H, td, J = 7.1, 0.9 Hz H_3), 7.35 (1H, td, J = 7.5, 1.1 Hz, H_7), 7.44 (1H, td J = 7.5, 1.1 Hz, H_6), 7.65 (1H, dd, J = 7.1, 0.9 Hz,H_4), 7.73 (1H, dd, J = 7.1, 0.9 Hz, H_1), 7.76 (1H, dd, J = 7.5, 1.1 Hz, H_5), 7.90 (1H, dd, J = 7.5, 1.1 Hz, H_8).

2b. In a manner similar to that mentioned above, **2b** was obtained in 83% yield as an *E/Z* mixture (= 57/43 by ^{1}H NMR): Mp 221— 224.5 °C (lit,[8] mp 214 °C); ^{1}H NMR of *E* form, δ = 6.71 (2H, s, NH_2), 7.39—7.47 (2H, m, H_6, H_7), 7.78 (1H, d, J = 8.1 Hz, H_4), 7.88—7.93 (1H, m, H_5), 7.94—7.98 (1H, m, H_8), 8.25 (1H, dd, J = 8.1, 2.1 Hz, H_3), 8.61 (1H, d, J = 2.1 Hz, H_1); ^{1}H NMR of *Z* form, δ = 6.70 (2H, s, NH_2), 7.48—7.57 (2H, m, H_6, H_7), 7.75—7.79 (1H, m, H_5), 7.80—7.84 (1H, m, H_8), 7.88 (1H, d, J = 8.1 Hz, H_4), 8.38 (1H, dd, J = 8.1, 2.1 Hz, H_3), 8.77 (1H, d, J = 2.1 Hz, H_1).

2e. Obtained in 89% yield as an *E/Z* mixture (= 77/23): Mp 249—252 °C (decomp) (lit,[10] mp 250—252 °C, decomp); ^{1}H NMR (DMSO-d_6) of *Z* form, δ = 8.18 (1H, d, J = 8.6 Hz, H_6), 8.35 (1H, d, J = 8.6 Hz, H_5), 8.63 (1H, s, H_8), 8.64 (1H, s, H_3), 9.17 (1H, s, H_1), 9.82 (2H, s, NH_2); ^{1}H NMR (DMSO-d_6) of *E* form, δ = 7.97 (1H, d, J = 8.6 Hz, H_6), 8.28 (1H, d, J = 8.6 Hz, H_5), 8.42 (1H, s, H_1), 8.79 (1H, s, H_3), 9.35 (1H, s, H_8), 9.82 (2H, s, NH_2).

2c. A mixture of 2,7-dinitrofluorenone (2.70 g, 10 mmol) and hydrazine hydrate (1.0 ml, 16.5 mmol) in AcOH (50 ml) was stirred at 80—85 °C for 5h, giving 1.99 g (70%) of **2c**: Mp > 283°C (decomp) (from AcOEt)(lit,[9] mp 275—278 °C, decomp); ^{1}H NMR (DMSO-d_6)δ = 8.24 (1H, d, J = 8.4 Hz, H_4), 8.32 (1H, d, J = 8.1 Hz, H_5), 8.35 (1H, m, H_3), 8.40—8.42 (2H, m, H_1, H_6), 9.16 (1H, bs, H_8), 9.27 (2H, bs, NH_2).

2d. Obtained in 93% yield by a similar procedure to above from 3,6-dinitrofluorenone: Mp > 275°C (decomp); ^{1}H NMR (DMSO-d_6) δ = 7.87 (1H, d, J = 8.4 Hz, H_1), 8.24 (1H, dd, J = 8.4, 2.0 Hz, H_2), 8.31 (1H, dd, J = 8.6, 2.1 Hz, H_7), 8.50 (1H, d, J = 8.6 Hz, H_8), 9.10 (1H, d, J = 2.0 Hz, H_4), 9.16 (1H, d, J = 2.1 Hz H_5), 9.61 (2H, bs, NH_2); MS *m/z* 284 (M^+). Found: C, 55.35; H, 2.70%. Calcd for $C_{13}H_8N_4O_4$: C, 54.93; H, 2.84%.

***p*-Hexyloxybenzaldehyde Azine (3).** Refluxing of the solution of *p*-hexyloxybenzaldehyde (0.62 g, 3 mmol) and hydrazine hydrate (0.2 ml, 5.1 mmol) in EtOH (30 ml) afforded 0.47 g (77%) of **3**: Mp

128.5—151 °C (cyclohexane) (lit,[17]) mp 127—153 °C); ^{1}H NMR $\delta=0.91$ (6H, t, $J=7.1$ Hz, Me), 1.32—1.50 (12H, m), 1.81 (4H, q, $J=6.5$ Hz), 4.01 (4H, t, $J=6.5$ Hz, OCH_2), 6.95 (4H, dd, $J=6.8$, 0.8 Hz, H_m), 7.64 (4H, $J=6.8$, 0.8 Hz, H_o), 8.61 (2H, s, N=CH).

9-[*p*-(Hexyloxy)benzylidenehydrazono]fluorene (4, R=C_6H_{13}). A suspension of **2a** (0.19 g, 1.0 mmol) in EtOH (30 ml) was refluxed for 8h with *p*-hexyloxybenzaldehyde (0.31 g, 1.5 mmol). Upon cooling, the precipitate was collected by filtration, washed with water, and recrystallized from ethanol to give 0.32 g (84%) of **4** (R = C_6H_{13}): Mp 93.5—94.5 °C; UV (CH_2Cl_2) λ_{max} 258 (log ε 4.67), 265 (4.66), 361 nm (4.46); UV (MeCN) λ_{max} 256 (log ε 4.67), 263 (4.64), 360 nm (4.47); ^{1}H NMR $\delta=0.93$ (3H, t, $J=6.7$ Hz, Me), 1.32—1.53 (6H, m), 1.84 (2H, q, $J=6.7$ Hz), 4.04 (2H, t, $J=6.7$ Hz, OCH_2), 7.01 (2H, dd, $J=8.9$, 2.0 Hz, H_m), 7.31 (1H, td, $J=7.5$, 0.9 Hz, H_7), 7.31 (1H, td, $J=7.5$, 0.9 Hz, H_2), 7.41 (1H, td, $J=7.5$, 0.9 Hz, H_6), 7.42 (1H, td, $J=7.6$, 0.9 Hz, H_3), 7.61 (1H, dd, $J=7.5$, 0.9 Hz, H_5), 7.63 (1H, dd, $J=7.6$, 0.9 Hz, H_4), 7.88 (2H, dd, $J=8.9$, 2.0 Hz, H_o), 7.92 (1H, dd, $J=7.6$, 0.9 Hz, H_8), 8.55 (1H, s, N=CH), 8.55(1H, dd, $J=7.5$, 0.9 Hz, H_1); MS *m/z* 382 (M^+). Found: C, 81.64; H, 6.85; N, 7.32%. Calcd for $C_{26}H_{26}N_2O$: C, 81.53; H, 6.62; N, 7.34%.

5 (R = C_6H_{13}). In a manner similar to that mentioned above, **5** (R = C_6H_{13}) was obtained in 56% yield; mp 174—175 °C (AcOEt); UV (CH_2Cl_2) λ_{max} 295 (log ε 4.47), 354 (4.48), 410 nm (s); ^{1}H NMR $\delta=0.93$ (3H, t, $J=6.7$ Hz, Me), 1.36—1.53 (6H, m), 1.84 (2H, q, $J=6.8$ Hz), 4.08 (2H, t, $J=6.8$ Hz, OCH_2), 7.09 (2H, dd, $J=6.8$, 2.0 Hz, H_m), 7.90 (1H, d, $J=6.3$ Hz, H_5), 7.93 (1H, d, $J=6.3$ Hz, H_4), 7.99 (2H, dd, $J=6.8$, 2.0 Hz, H_o), 8.41 (1H, dd, $J=6.3$, 2.0 Hz, H_6), 8.44 (1H, dd, $J=6.3$, 2.0 Hz, H_3), 8.75 (1H, s, N=CH), 8.86 (1H, d, $J=2.0$ Hz, H_8), 9.70 (1H, d, $J=2.0$ Hz, H_1); MS *m/z* 472(M $^+$). Found: C, 66.44; H, 4.78; N, 11.65%. Calcd for $C_{26}H_{24}N_4O_5$: C, 66.09; H, 5.12; N, 11.86%.

5 (R = C_4H_9). Found: C, 65.10; H, 4.37; N, 12.63%. Calcd for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.61%.

5 (R = C_5H_{11}). Found: C, 65.74; H, 4.57; N, 11.87%. Calcd for $C_{25}H_{22}N_4O_5$: C, 65.49; H, 4.84; N, 12.22%.

6 (R = C_6H_{13}). Similarly, **6** (R = C_6H_{13}) was obtained in 52% yield; mp 229 —230 °C (AcOEt); ^{1}H NMR $\delta=0.93$ (3H, t, $J=6.6$ Hz, Me), 1.34—1.56 (6H, m), 1.85 (2H, q, $J=6.6$ Hz), 4.08 (2H, t, $J=6.6$ Hz, OCH_2), 7.06 (2H, dd, $J=6.9$, 1.8 Hz, H_m), 7.93 (2H, dd, $J=6.9$, 1.8 Hz, H_o), 8.14 (1H, d, $J=8.7$ Hz, H_8), 8.33 (1H, dd, $J=8.4$, 2.1 Hz, H_2), 8.34 (1H, dd, $J=8.7$, 1.2 Hz, H_7), 8.59 (1H, s, H_5), 8.60 (1H, s, H_4), 8.71 (1H, s, N=CH), 8.90 (1H, dd, $J=8.4$, 2.1 Hz, H_1); MS *m/z* 472 (M^+). Found: C, 66.40;H, 5.02; N, 11.75%. Calcd for $C_{26}H_{24}N_4O_5$: C, 66.09; H, 5.12; N, 11.86%.

6 (R = C_7H_{15}). Found: C, 66.60; H, 5.02; N, 11.19%. Calcd for $C_{27}H_{26}N_4O_5$: C, 66.65; H, 5.39; N, 11.52%.

6 (R = C_8H_{17}). Found: C, 67.41; H, 5.31; N, 10.80%. Calcd for $C_{28}H_{28}N_4O_5$: C, 67.18; H, 5.64; N, 11.11%.

6 (R = C_9H_{19}). Found: C, 67.47; H, 5.81%. Calcd for $C_{29}H_{30}N_4O_5$: C, 67.69; H, 5.88%.

7 (R = C_6H_{13}). **7**(R = C_6H_{13}) was obtained in 0.31 g (83%) yield as a configurational isomeric mixture (*EE*/*ZE* = 56/44) by the reaction of **2b** (0.20 g, 0.83 mmol) with *p*-hexyloxybenzaldehyde in ethanol (20 ml): Mp 104—114 °C. The mixture was dissolved into AcOEt and evaporated below 5 °C. Orange crystals were collected and recrystallized from EtOH to give 0.10 g (27%) of *EE*-form: Mp 130.5—133.0 °C; UV (CH_2Cl_2) λ_{max} 245 (log ε 4.53), 296 (4.46), 374 nm (4.53); ^{1}H NMR $\delta=0.93$ (3H, t, $J=7.2$ Hz, Me), 1.34—1.52 (6H, m), 1.84 (2H, q, $J=7.2$ Hz), 4.06 (2H, t, $J=7.2$ Hz, OCH_2), 7.03 (2H, dd, $J=6.9$, 2.1 Hz, H_m), 7.46(1H, td, $J=7.5$, 1.2 Hz, H_6), 7.51 (1H, td, $J=7.5$, 1.2 Hz, H_7), 7.73 (1H, dd, $J=8.2$, 2.1 Hz, H_4), 7.75 (1H, dd, $J=7.5$, 1.2 Hz, H_5), 7.90 (2H, dd, $J=6.9$, 1.8 Hz, H_o), 8.32 (1H, dd, $J=8.2$, 1.8 Hz, H_3), 8.61 (1H, s, N=CH), 8.65 (1H, dd, $J=7.5$, 1.2 Hz, H_8), 8.74 (1H, d, $J=1.8$ Hz, H_1).

Lemon-yellow crystals were collected and recrystallized from EtOH to yield 0.03 g (8%) of *ZE*-form: Mp 130.0—132.5 °C; UV (CH_2Cl_2) λ_{max} 243 (log ε 4.50), 306 (4.38), 341 (4.46), 378 nm (4.43); ^{1}H NMR $\delta=0.93$ (3H, t, $J=7.2$ Hz, Me), 1.34—1.52 (6H, m), 1.84 (2H, q, $J=7.2$ Hz), 4.07 (2H, t, $J=7.2$ Hz, OCH_2), 7.06 (2H, dd, $J=6.9$, 2.1 Hz, H_m), 7.43 (1H, td, $J=7.5$, 1.2 Hz, H_7), 7.50 (1H, td, $J=7.5$, 1.2 Hz, H_6), 7.71 (1H, dd, *7.5*, 1.2 Hz, H_5), 7.73 (1H, dd, $J=8.4$, 1.2 Hz, H_4), 7.94 (2H, dd, $J=6.9$, 1.8 Hz, H_o), 7.98 (1H, dd, $J=7.5$, 1.2 Hz, H_8), 8.32 (1H, dd, $J=8.4$, 1.8 Hz, H_3), 8.66 (1H, s, N=CH), 9.58 (1H, d, $J=1.8$ Hz, H_1).

7 (R = C_7H_{15}). Found: C, 73.83; H, 5.95%. Calcd for $C_{27}H_{27}N_3O_3$: C, 73.45; H, 6.16%.

8 (R = C_6H_{13}). A suspension of **2e** (0.33 g, 1.0 mmol), *p*-hexyloxybenzaldehyde (0.31 g, 1.5 mmol) in THF (20 ml) was refluxed for 3 h with concentrated sulfuric acid (2 drops). Upon dilution with water, the deposit was washed with water, successively with EtOH, and recrystallized from dichloromethane to give 0.40 g (78%) of *EE/ZE* mixture (= 45/55) of **8** (R = C_6H_{13}): Mp 156—159 °C; UV (CH_2Cl_2) λ_{max} 285 (log ε 4.49), 360 (4.37), 425 nm (4.32); MS *m/z* 517 (M^+). Found: C, 60.21; H, 4.45; N, 13.65%. Calcd for $C_{26}H_{23}N_7O_5$: C, 60.35; H, 4.48; N, 13.53%.

^{1}H NMR for *EE* form, $\delta=0.95$ (3H, t, $J=6.4$ Hz, Me), 1.36—1.53 (6H, m), 1.85 (2H, q, $J=6.4$ Hz), 4.10 (2H, t, $J=6.4$ Hz, OCH_2), 7.10 (2H, dd, $J=7.6$, 2.1 Hz, H_m), 8.00 (2H, dd, $J=7.6$, 2.1 Hz, H_o), 8.34 (1H, d, $J=8.8$ Hz, H_5), 8.45 (1H, dd, $J=8.8$, 2.1 Hz, H_6), 8.80 (1H, s, N=CH), 8.90 (1H, d, $J=2.3$ Hz, H_3), 9.11 (1H, d, $J=2.3$ Hz, H_1), 9.85 (1H, d, $J=2.1$ Hz, H_8). ^{1}H NMR for *ZE* form, $\delta=0.95$ (3H, t, $J=6.4$ Hz, Me), 1.36—1.53 (6H, m), 1.85 (2H, q, $J=6.4$ Hz), 4.10 (2H, t, $J=6.4$ Hz, OCH_2), 7.10 (2H, dd, $J=7.6$, 2.2 Hz, H_m), 8.00 (2H, dd, $J=7.6$, 2.1 Hz, H_o), 8.23 (1H, dd, $J=8.8$, 2.3 Hz, H_6), 8.41 (1H, d, $J=8.8$ Hz, H_5), 8.78 (1H, s, N=CH), 8.88 (1H, d, $J=2.3$ Hz, H_3), 8.91 (1H, d, $J=2.3$ Hz, H_8), 10.14 (1H, d, $J=2.3$ Hz, H_1).

1 (R = NEt_2, R′ = H). A mixture of **2a** (194 mg, 1.0 mmol) and *p*-diethylaminobenzaldehyde (212 mg, 1.2 mmol) was heated at 155—160 °C for 5 min. The residue was chromatographed on silica gel with benzene to yield 177 mg (50%) of **1** (R = NEt_2, R′ = H); mp 142—143 °C; UV (CH_2Cl_2) λ_{max} 259 (log ε 4.62), 301 (4.18), 442 nm (4.52); UV (MeCN) λ_{max} 214 (log ε 4.48), 257 (4.62), 440 nm (4.54); MS *m/z* 353 (M^+), 338. Found: C, 81.70; H, 6.59; N, 11.82%. Calcd for $C_{24}H_{23}N_3$: C, 81.55; H, 6.56; N, 11.89%.

9a. Obtained in 56% yield; mp 153—154 °C; UV (CH_2Cl_2) λ_{max} 243 (log ε 4.41), 298 (4.40), 478 nm (4.48); UV (MeCN) λ_{max} 221 (log ε 5.24), 296 (4.40), 474 nm (4.48); MS *m/z* 398 (M^+), 383. Found: C, 72.38; H, 5.69; N, 13.85 %. Calcd for $C_{24}H_{22}N_4O_2$: C, 72.34; H, 5.57; N 14.06%.

9b. A 64% yield; mp 265—266 °C (decomp); UV (CH_2Cl_2) λ_{max} 251 (log ε 4.33), 295 (4.52), 329 (4.43), 520 nm (4.49); UV (MeCN) λ_{max} 215 (log ε 4.47), 248 (4.32), 294 (4.50), 328 (4.42), 506 nm (4.48); MS *m/z* 443 (M^+), 428. Found: C, 64.95; H, 4.69; N, 15.80%. Calcd for $C_{24}H_{21}N_5O_4$:C, 65.00; H, 4.77; N, 15.79%.

9c. An 80% yield; mp 251—252 °C (decomp); UV (CH_2Cl_2) λ_{max} 255 (log ε 4.40), 292 (4.47), 347 (4.37), 564 nm (4.49); UV (MeCN) λ_{max} 215 (log ε 4.46), 253 (4.34), 290 (4.43), 342 (4.33), 545 nm (4.44); MS *m/z* 488 (M^+), 473. Found: C, 58.75; H, 4.00; N, 16.93%. Calcd for $C_{24}H_{20}N_6O_6$: C, 59.01; H, 4.13; N, 17.21%.

We are grateful to Professor T. Kato and Mr. M. Ehara of Utsunomiya University for preparing and measuring the monolayers. We also thank Mr. O. Kimura and Mr. Y. Narabu for their preliminary experiments.

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