New Synthesis of *N,N*-Disubstituted (4-Aminophenyl)diazenyl-1,3,4-thiadiazole, and Mesogenic Study and Molecular Modeling of Its H-Bonded Complexes with a Series of *m*-Alkoxybenzoic Acid Derivatives

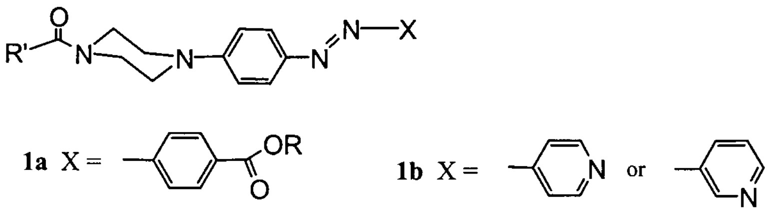
by **Long-Li Lai*** and **Eshin Wang**

Department of Applied Chemistry, National Chi Nan University, Puli, Taiwan 545, R.O.C.
(Tel: 886-49-2910960 ~ 4975, fax: 886-49-2917956; e-mail: lilai@ncnu.edu.tw)

A new *N*,*N*-disubstituted (4-aminophenyl)diazenyl-1,3,4-thiadiazole, an azo dye, was synthesized from the reaction of the 1-decanoyl-4-phenylpiperazine in acetone, *in situ*, with the diazonium salt prepared from 1,3,4-thiadiazol-2-amine and $NaNO_2$ in H_3PO_4. The azo dye was found to form complexes with a series of *m*-alkoxybenzoic acid by intermolecular H-bonding. The mesogenic behavior of the complexes were investigated by polarizing optical microscopy and differential scanning calorimetry. A study of the representing complex by powder X-ray diffraction and molecular modeling was further undertaken to locate the H-bonding position.

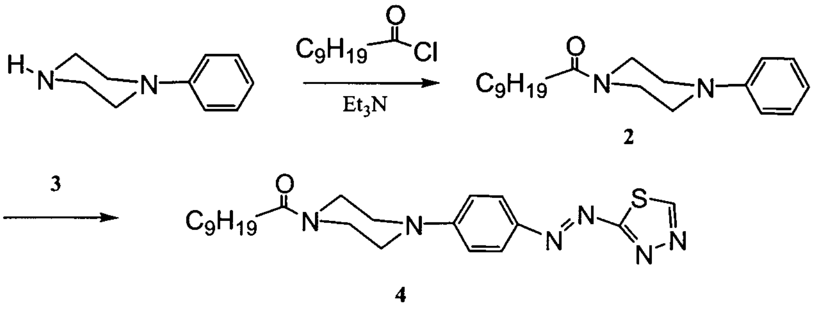
1. Introduction. – Azo-dye molecules have recently attracted a lot of attention in both academic and application areas [1][2], and, particularly, azo-dyes have a reasonable dichroic ratio and are suitable for the lower-power-consumption reflective liquid-crystal devices [3]. In a guest-host system (G-H), the dichroic dye is dissolved in a liquid crystal to give better reflectance of the polarizer [4]. In particular, three-layered G-H system with subtractive color mixing of yellow, magenta, and cyan are expected to be used for developing the full-color reflective displays [5]. However, the solubility and the phase-transition temperatures of the G-H systems are serious problems for application. Usually, the clearing temperatures vary with the components of the G-H systems, and addition of the nonmesogenic dyes often causes instability of the liquid-crystalline phase [6]. Dyes that are themselves mesogenic minimize this effect, and, therefore, azo-dye liquid crystals are highly desirable as dopants.

Previously, we have synthesized a series of crystalline yellow azo-dye molecules, **1a**, containing an electron-donating amino function and an electron-withdrawing carboxylate group [7]. To obtain further compounds with magenta or cyan colors, *i.e.*, to further decrease the LUMO-HOMO energy gap of the molecules, we can synthesize compounds with stronger electron-withdrawing groups, such as CN or NO_2, to replace the carboxylate moiety. Although we can achieve this purpose by such a strategy, the diversity of the liquid-crystalline molecules is, however, to some extent, limited, as the CN and NO_2 groups are short, and no further attachments can be linked on them. Moreover, enhancement of the variation between the donor and acceptor on each end also, to some extent, destabilizes the molecule, as the charge density is accumulated. In the field of optical and electrical materials, thermal stability is one of the most important factors to be considered in the design of molecules. Therefore, we tried to reduce the LUMO-HOMO energy gap of the molecules by introducing a heteroaromatic system, such as a pyridine ring, to replace the benzenecarboxylate moiety. By this strategy, we have synthesized pyridine-containing azo dyes with the structure **1b**, which shows a yellow color [8], and the UV/VIS absorption (λ_{max}) is 415 nm in CH_2Cl. We now further synthesize *N*,*N*-disubstituted 2-[(4-aminophenyl)diazenyl]-1,3,4-thiadiazoles and study their mesogenic behaviors on the H-bonded complexes with a series of *m*-alkoxybenzoic acids. Although the thermomesomorphic H-bonded complexes between pyridyl derivatives and carboxylic acids have been investigated [9], the thermomesomorphic properties between the thiadiazole and benzoic acid derivatives have not yet been studied.



Results and Discussion. – Compound **2** was prepared in almost quantitative yield by the reaction of *N*-phenylpiperazine with decanoyl chloride in CH_2Cl_2 in the presence of Et_3N. The *N*,*N*-disubstituted 2-[(4-aminophenyl)diazenyl]-1,3,4-thiadiazole **4** was synthesized from compound **2** and diazonium salt **3** according to *Scheme 1*. The corresponding diazonium salt **3** according to *Scheme 2* was found to be efficiently prepared according to a described method [10]. However, by this procedure, another major product (instead of compound **4**) was isolated, which was assumed to have structure **5** by ^{1}H-NMR[1]). For further identification, compound **2** was treated with a mixture of HNO_3/H_2SO_4 1:1, and a nitration product from **2** was isolated, which shows the same ^{1}H-NMR spectrum as compound **5**. According to the literature, the nitrate counter ion was added to stabilize the diazonium salt. However, in such a reaction, nitration of the electron-rich aromatic ring also takes place. This may explain why, in our reaction, a significant amount of compound **5** was isolated. To avoid this side

Scheme 1



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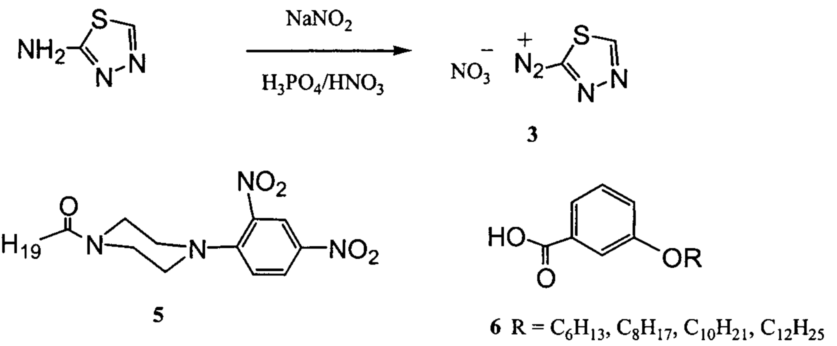
[1]) ^{1}H-NMR for **5**: 0.84 (*t*, *J* = 6.6, CH_3); 1.20–1.38, 1.58–1.62 (2*m*, 7 CH_2); 2.32 (*t*, *J* = 6.9, CH_2); 3.42 (br. *s*, 2 CH_2); 3.60 (*t*, 2 H, *J* = 5.1, CH_2), 3.72 (*t*, *J* = 5.1, CH_2); 6.82 (*d*, *J* = 9.2, 1 arom. H); 8.27 (*dd*, *J* = 9.2, 2.7, 1 arom. H), 8.69 (*d*, *J* = 2.7, 1 arom. H).

Scheme 2



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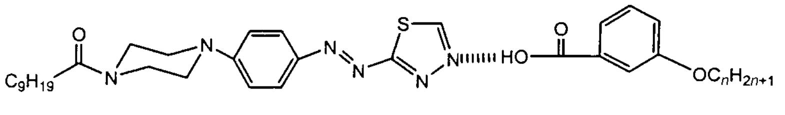
5

6 R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$

reaction (nitration) and improve the yield of the desired azo dye **4**, acetone (instead of HNO_3) was used to increase the solubility of the reactants in H_3PO_4, and compound **4** was isolated in *ca.* 33% yield after purification. The UV/VIS absorption band (λ_{max}) of **4** is 466 nm in CH_2Cl_2. The absorption band is found to have a red-shift of *ca.* 50 nm, when compared with that of compound **1b**.

The H-bonded complexes **S2N-m-ABn** were prepared from the azo dye **4** with 1 equiv. of *m*-alkoxybenzoic acids **6** ($n = 6$, 8, 10, 12). Compound **4** shows a SmC phase in the heating and cooling processes (*Table 1*). The alkoxybenzoic acid derivatives

Table 1. *Phase-Transition Temperature and Corresponding Enthalpies* ([J g^{-1}], in parentheses) *of H-Bonded Complexes from a 1:1 Molar Ratio of* **4** *and* m-*Alkoxybenzoic acid* **6** ($n = 6$, 8, 10, 12)[a])



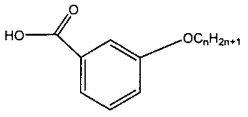
S2N-m-ABn

4	Cr	$\underset{100.3(38.6)}{\overset{144.7(38.1)}{\rightleftharpoons}}$	SmC	$\underset{153.6(9.2)}{\overset{155.4(4.6)}{\rightleftharpoons}}$			I
S2N-m-AB6	Cr			$\underset{61.1(22.0)}{\overset{99.0(26.5)}{\rightleftharpoons}}$	SmA	$\underset{125.3}{\overset{129.5}{\rightleftharpoons}}$	I
S2N-m-AB8	Cr	$\xrightarrow{67.4(4.3)}$	SmX	$\underset{61.4(19.5)}{\overset{97.3(27.3)}{\rightleftharpoons}}$	SmA	$\underset{129.7}{\overset{133.2}{\rightleftharpoons}}$	I
S2N-m-AB10	Cr	$\xrightarrow{67.4(4)}$	SmX	$\underset{61.7(26.0)}{\overset{97.4(27.5)}{\rightleftharpoons}}$	SmA	$\underset{143.8}{\overset{149.0}{\rightleftharpoons}}$	I
S2N-m-AB12	Cr	$\underset{56.6(1.8)}{\overset{83.4(2)}{\rightleftharpoons}}$	SmX	$\underset{64.5(8.3)}{\overset{93.3(7.9)}{\rightleftharpoons}}$	SmA	$\underset{127.2}{\overset{130.3}{\rightleftharpoons}}$	I

[a]) The phase-transition temperatures and corresponding enthalpies of the H-bonded complexes were determined by 2nd scans of differential scanning calorimetry with *Perkin-Elmer DSC-6* at a heating and cooling rate of 10°/min between 50 and 170°. Abbreviations: Cr = crystalline, SmC = smectic C phase, SmX = unidentified phase, SmA = smectic A phase, I = isotropic liquid. The clearing point from SmA phase to isotropic was recorded by polarizing optical microscopy.

6 ($n = 6, 8, 10$) do not show any liquid-crystalline properties during their heating and cooling processes (*Table 2*). Compound **6** ($n = 12$) shows two crystalline types during the heating process and two crystalline types and one highly ordered smectic phase during the cooling process. However, the H-bonded complexes **S2N-m-ABn** show a SmA phase and highly-ordered mesogenic phases during the heating and cooling processes. The mesogenic behaviors of the complexes **S2N-m-ABn**, different from those of the azo dye **4** and the acids **6**, are induced through the intermolecular H-bonding. The SmC phase of **4** was characterized by the broken focal-conic texture that co-exists with the *schlieren* texture by polarizing optical microscopy. The complexes **S2N-m-ABn** under polarizing optical microscope show a focal-conic fan texture, co-existing with the homeotropic alignment, which was characterized as a SmA phase and further confirmed by the powder X-ray diffraction.

Table 2. *Phase-Transition Temperature and Corresponding Enthalpies* ([J g^{-1}], in parentheses), *of* m-*Alkoxybenzoic acid* ($n = 6, 8, 10, 12$)[a]



m-alkoxybenzoic acid **6**

$n = 6$	Cr	$\underset{48.9(102.5)}{\overset{69.8(102.2)}{\rightleftharpoons}}$			I
$n = 8$	Cr	$\underset{60.9(133.5)}{\overset{73.9(132.3)}{\rightleftharpoons}}$			I
$n = 10$	Cr	$\underset{56.3(123.8)}{\overset{71.9(121.7)}{\rightleftharpoons}}$			I
$n = 12$	Cr	$\underset{68.9(5.8)}{\overset{76.2(5.1)}{\rightleftharpoons}}$	Cr1	$\xrightarrow{89.1(109.7)}$ $\xleftarrow[76.5]{}$ SmX $\xleftarrow[79.6^{b)}]{}$	I

[a] The phase-transition temperatures and corresponding enthalpies of compound **6** were determined by 2nd scans of differential scanning calorimetry with *Perkin Elmer DSC-7* at a heating and cooling rate of 10°/min, between 50 and 150°. Abreviations: Cr = crystalline, SmX = unidentified smectic phase, I = isotropic liquid. [b] The peaks are overlapped, and their total enthalpy is 121.2 J g^{-1}.

The *d*-spacing distances (the Z component of an extended molecular length) of the complex **S2N-m-AB8** from the X-ray-diffraction study in the SmA phase are 40.49 Å at 80°, 39.95 Å at 100°, and 38.60 Å at 120° during the cooling. The *d*-spacing decreases gradually while temperature rises. This may arise from the greater vibration of the molecules at higher temperature in the solid state, and the gap between the molecular layers becomes closer. The X-ray pattern in the SmA range showed only a sharp reflection in the small-angle region, indicating a smectic layer structure without regular arrangement within the layers. Although we change the tail lengths of the acids **6**, the mesogenic range for complexes **S2N-m-ABn** from smectic A to isotropic liquid or SmX phases do not vary much from each other. The range of SmA is *ca.* 60–70° for these H-bonded complexes.

As compound **4** contains six N- and one S-atoms, it is interesting to know whether an N- or the S-atom is involved in H-bonding with the *m*-alkoxybenzoic acid. The electron surface of model molecule **7** was calculated by CAChe program, and the charge distribution for the thiadiazole ring is shown below. The partial negative charges are distributed over N(3), N(4), and C(5), and the partial positive charges are distributed over S(1) and C(2). We, thus, reasonably suggest that the intermolecular interaction can occur between N(4) of **4** and carboxyl H-atoms of **6** ($n = 8$), as well as possibly H−C(5) of **4** and C=O of **6**. The molecular-modeling study reveals a calculated distance between the N(4) of **4** and carboxy H-atom of **6** ($n = 8$) of 1.81 Å. Similarly, the distance between the H−C(5) of **4** and C=O of **6** ($n = 8$) is calculated to be 2.43 Å. This interaction lowers the energy of the system by 2.43 kcal/mol[2]. Significantly, the distance between C(a) of **6** ($n = 8$) and C(b) of **4** is calculated to be 38.97 Å (*Fig.*), which is slightly longer than the *d*-spacing obtained from the X-ray-diffraction study (37.94 Å at 25°). As the simulation of the molecule was carried out in vacuum, the optimized conformation is similar to that of the molecule in gas phase. However, the polarity of the structure **7** can be reasonably applied to intermolecular interaction in the solid state in our case, as the polarity of the molecule should maintain consistency in gas, liquid, and solid phases. The calculated H-bond distances between the azo dye **4** and the acids **6** can be greater than those in the complexes in the real situation, as the vibration of the molecules should be smaller in the solid state. That may also explain that our calculated distance is slightly greater than the *d*-spacing obtained from the X-ray-diffraction study.

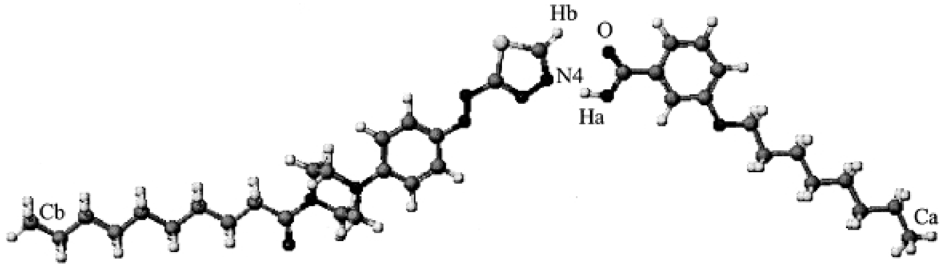
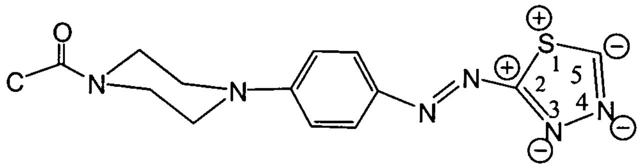


Figure. *Molecular modeling involving compounds* **4** *and* **6** ($n = 6$)



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In conclusion, this work presents a successful approach to induce mesogenic heterocycle-containing azo-dye complexes through intermolecular H-bonding. This approach may open another useful azo-dye liquid-crystal area. The mesogenic

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[2] The energy of **4**, **6** ($n = 8$), and **S2N-m-AB8** structures are 53.06, −139.33, and −88.70 kcal/mol, respectively (*Fig. 2*).

behaviors of other heterocycle-containing azo dyes with narrower HOMO-LUMO energy gaps may be induced similarly.

Experimental Part

General. Chemicals used were commercially available from *ACROS. m*-Alkoxybenzoic acids **6** were synthesized according to literature methods [9]. The H-bonded complexes **S2N-m-ABn** were prepared by dissolving the azo dye and benzoic acid derivatives in a 1:1 ratio in sufficient amounts of THF. The resulting soln. was then kept in a fume hood for 48 h, while THF was allowed to evaporate spontaneously. The resulting solid was ground and thoroughly blended before studying the liquid-crystalline properties. UV Spectra (λ_{max}): HP 8453 spectrometer. IR Spectra: [cm^{-1}]: *Perkin-Elmer FTIR-1000* spectrometer. ^{1}H- and ^{13}C-NMR Spectra: *Varian 300-FT* and *Bruker 300-FT* spectrometers, resp. EI-HR-MS: 70 eV; *VG70-250*. The mesogenic behaviors and phase transitions were characterized by polarizing optical microscopy and differential scanning calorimetry (*Perkin-Elmer DSC 6*). Powder X-ray diffraction (XRD) patterns were obtained with a *Siemens D-5000* X-ray diffractometer equipped with a *TTK 450* temp. controller and Cu radiation with the wavelength length λ = 1.5406 Å. Semiempirical calculations were carried out with the CAChe program, which was provided by *Fujitsu* (Japan). The structure of the compound **7** and complex **S2N-m-AB8** were optimized by performing an geometry calculation in mechanics with augmented MM3 parameters and further refined by calculating the optimized geometry by MOPAC with PM3 parameters.

Synthesis of 2-{[4-(4-Decanoylpiperazin-1-yl)phenyl]diazenyl}-1,3,4-thiadiazole (**4**). – 2-Amino-1,3,4-thiadiazole (1.01 g, 10 mmol) was dissolved in H_3PO_4 (20 ml), and $NaNO_2$ (1.03 g, 15 mmol) was gradually added at 0° to produce the diazonium salt **3**. The phenylpiperazine derivative **2** (3.16 g, 10 mmol) in acetone (10 ml) was then added. The soln. was stirred for 2 h, while the temp. gradually rose. Then, H_2O (100 ml) was added, and the mixture was extracted with CH_2Cl_2 (2 × 100 ml). The combined extracts were dried (Na_2SO_4), and solvent was removed under reduced pressure. Acetone (5 ml) was added, and the solid, which had precipitated, was filtered off, washed with acetone (2 ml), and dried. The azo dye **4**, after purification by chromatography for the further physical study, was obtained in 33.8% yield (1.32 g). UV/VIS (CH_2Cl_2): λ_{max} 466. IR: 2928, 2856, 1645, 1600, 1513, 1439, 1379, 1276, 1207, 1152. ^{1}H-NMR ($CDCl_3$): 0.85 (*t*, *J* = 6.3, Me); 1.18–1.40, 1.58–1.63 (2*m*, 7 CH_2); 2.35 (*t*, *J* = 6.9, CH_2); 3.50 (br. *s*, 2 CH_2); 3.66 (*t*, *J* = 5.1, CH_2); 3.80 (*t*, *J* = 5.1, CH_2); 6.91 (*AA'BB'*, *J* = 9.3, 2 arom. H); 7.96 (*AA'BB'*, *J* = 9.3, 2 arom. H); 9.01 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 171.98 (C=O); 154.25; 152.01; 151.76; 127.18; 114.47; 47.82; 47.58; 47.25; 33.26; 31.84; 29.44; 29.25; 25.20; 22.63; 14.08. HR-MS: 428.2858 ($C_{22}H_{32}N_6OS$; calc. 428.2361).

Compound **4** was further characterized by single-crystal structure determination, and the result will be published elsewhere.

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