Single Crystal Structure Determination and Molecular Modeling of Ethyl 4-[[4-(dodecanoyloxy)phenyl]diazenyl]benzoate; Various Mesogenic Behaviors from Different Lengths of Alkyl Chains

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The molecular stacking and conformation of ethyl 4-[[4-(dodecanoyloxy)phenyl]diazenyl]benzoate was established on the basis of crystallographic data and further compared with those of 4-[[4-(decanoyloxy)phenyl]diazenyl]benzoate and 4-[[4-(octanoyloxy)phenyl]diazenyl]benzoate. The variation of mesogenic behaviors resulting from the different lengths of alkyl chains was also studied.

Key words: Liquid crystal; Azo dye; Single crystal structure determination and molecular simulation.

INTRODUCTION

Supramolecular aggregation by molecular self-assembly is an important issue in the field of structural chemistry.¹ In addition to electrostatic interaction, non-covalent forces also play a significant role in determining the structural stacking and properties of molecular assemblies.² The interaction between molecules containing functionalities is found to be critical for molecular packing in crystallization³ and for the varying mesogenic behaviour of the molecules.⁴ Azo dyes **1a** and **1b** have previously been prepared⁵ and their liquid crystalline phases also studied in this laboratory: We found that the various conformations of the molecules resulted in various molecular stackings in the solid state and different mesogenic phases were obtained in this way, namely, **1a** with a C₇H₁₅ chain showing nematic and SmA phases and **1b** with a C₉H₁₉ chain showing a SmB phase during the thermal process. As this observation is so unusual, we further prepared **1c** and **1d** and studied their mesogenic behaviours. Azo dye **1d** with a C₁₁H₂₃ chain was further studied by single crystal structure determination. The corresponding molecular stacking in the solid state was thus established, investigated and further compared with those of **1a** and **1b**. The conformation of **1d** in the gas phase was also studied by molecular modeling and compared with those of **1a** and **1b**. Now we wish to report all

these results.

EXPERIMENTAL

Chemicals used were commercially available from ACROS. The mesogenic behaviour and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 6). Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller and Cu radiation with the wavelength length, $\lambda = 1.5406 \text{ \AA}$. Semi-empirical calculation was carried out by the Cache program using the AM1 model, which was provided by Fujitsu (version 4.1).

Synthesis of Compounds **1c** and **1d**

Azo dyes **1c** and **1d** were prepared by a similar manner according to the reaction scheme, confirmed and characterized by spectroscopy ¹H-NMR (Varian 300 FT spectrometer) and high resolution mass spectra (HRMS; VG70-250; EI, 70 eV). Compound **2** (0.54 g, 2 mmol), prepared according to a previous procedure,⁵ was further treated with hexanoyl chloride (0.33 g, 2 mmol) in dichloromethane (20 mL) with an excess of triethylamine to yield crude product **1c**, which was further purified by chroma-

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Reaction scheme

tography (Al₂O₃; II); it amounted to 0.48 g (65.5%) after normal work-up. ¹H-NMR (CDCl₃): δ 0.90 (t, 3H, *J* = 6.9 Hz, CH₃), 1.33–1.43 (m, 7H, 2CH₂+CH₃), 1.77 (quint, 2H, CH₂), 2.58 (t, 2H, *J* = 7.2 Hz, CH₂), 4.40 (quart, 2H, CH₂), 7.25 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.92 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.97 (d, 2H, *J* = 8.7 Hz, Ar-H), 8.17 (d, 2H, *J* = 8.7 Hz, Ar-H). HRMS for C₂₁H₂₄N₂O₄: 368.1736. Found: 368.1738. Compound **1d** (0.62 g, 69.3%) was prepared similarly. ¹H-NMR (CDCl₃): δ 0.85 (t, 3H, *J* = 6.9 Hz, CH₃), 1.25–1.44 (m, 19H, 8CH₂+CH₃), 1.76 (quint, 2H, CH₂), 2.58 (t, 2H, *J* = 7.2 Hz, CH₂), 4.41 (quart, 2H, CH₂), 7.25 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.91 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.96 (d, 2H, *J* = 8.7 Hz, Ar-H), 8.17 (d, 2H, *J* = 8.7 Hz, Ar-H). HRMS for C₂₇H₃₆N₂O₄: 452.2675. Found: 452.2678.

X-ray Crystallography Analysis

Crystals of compound **1d** were grown from dichloromethane/hexane (1/1) at room temperature. A single orange crystal of suitable quality was mounted on a glass fiber and used for measurement of precise cell constants and intensity data collection. Diffraction measurement was made on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), operated at 295(2) K over the θ range of 1.06–25.00°. No significant decay was observed during the data collection. 2850 reflections were observed with *I* ≥ 2σ(*I*) among the 11331 unique reflections, and 7434 reflections were used in the refinement. Data were processed on a PC using the *SHELXTL* software package.⁶ The structure of **1d** was solved using direct methods and refined by full-matrix least square on an *F*² value. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were identified by calculation, and their contributions in

structure factors were included. The final indices were *R*₁ = 0.1043, *wR*₂ = 0.2572 with goodness-of-fit on *F*² = 1.059. Other data are described as follows: formula C₂₇H₃₆N₄O₂; formula weight 452.27; crystal size 0.20 × 0.15 × 0.10 mm³; unit cell *a* = 5.9860(7), *b* = 7.6040(9), *c* = 57.628(7), α = 91.461(2), β = 92.582(3), γ = 92.404(3); crystal system triclinic; space group *P*-1; volume 2617.1(5) Å³; cell units (*Z*) 4; density (calcd.) 1.154 g cm⁻³; linear absorption coefficient 0.077 (μ/cm⁻¹). Crystallographic data for the compound **1d** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-267498. Copies of the data can be obtained free of charge on publication to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION**Synthesis and physical study**

Reaction of phenol with diazonium salt **2** in basic conditions gave compound **3** in ~45% yield, and further treatment of compound **3** with the corresponding acyl chlorides yielded the desired azo dyes **1c** and **1d** in approx. 65% yields. It was found that this series of azo dyes were not chemically stable in acid media but thermally stable during the thermal process. Azo dye **1c**, like **1a**, showed nematic and SmA phases during the cooling process (Table 1). However, azo dye **1d**, unlike **1b** with the SmB phase, showed a SmA phase during the thermal process. The nematic phase was characterized by its schlieren texture; the SmA phase was characterized by a typical focal-conic texture (Fig. 1). To confirm the nematic and SmA phases of azo dyes **1c** and **1d**, respectively, they were further studied by powder XRD. As there is no layer structure in the nematic phase during the cooling, no reflection at small angle was observed for azo dye **1c** at 81.6–66.7 °C. The nematic phase of azo dye **1a** was confirmed by powder XRD as indicated previously.^{5a} Also, the d-spacing distance (the z-component of an extended molecular length) for compound **1d** at 87 °C was measured as 31.95 Å obtained by powder XRD during the cooling process; the extended molecular length of compound **1d** was calculated to be 31.45 Å between two ending hydrogens by the Cache program on the basis of molecular conformation from the crystallographic data. As liquid crystal molecules in the SmA range are directed along the *z*-axis, the d-spacing from the XRD study

Table 1. Phase transition temperature and corresponding enthalpies (KJ/mole), in parentheses, of compounds **1a-1b**

1a , R = C ₇ H ₁₃	Cr	$\xrightleftharpoons[68.1(142.9)]{83.3^a}$	SmA	$\xrightleftharpoons[78.3(25.2)]{87.3^a(212.9)}$	SmX N	$\xrightleftharpoons[85.3(4.7)]{87.3^a(212.9)}$	I
1b , R = C ₉ H ₁₉					SmB ^d	$\xrightleftharpoons[88.4(229.2)]{95.3(230.9)}$	I
1c , R = C ₅ H ₁₁	Cr	$\xrightleftharpoons[63.6(150.0)]{81.6^b}$	SmA	$\xrightleftharpoons[66.7(7.8)]{82.7^b(170.7)}$	N	$\xrightleftharpoons[81.6(4.1)]{82.7^b(170.7)}$	I
1d , R = C ₁₁ H ₂₃	Cr	$\xrightleftharpoons[75.5(141.8)]{90.3^c}$	SmA			$\xrightleftharpoons[91.3(39.1)]{93.1^c(214.4)}$	I

Abbreviations: Cr = crystalline, SmX = unidentified smectic phase, N = nematic, SmA = smectic A phase, SmB = smectic B phase, I = isotropic liquid.

^{a,b,c} peaks overlapped

^d the SmB phase of compound **1b** remained even at room temperature

should be approximately equal to the fully extended length of the molecule; therefore, our experimental results are consistent with each other. Additionally, as it is so unusual that azo dye **1b** possesses a SmB phase during the thermal process (Figs. 2a and 2b), reconfirmation of its mesogenic behaviour is necessary. Compared with azo dye **1d**, the enthalpy change of azo dye **1b** from liquid crystalline to

Fig. 1. The texture of azo dye **1d** at 85 °C during the cooling process.

isotropic states is much higher. As shown in Table 1, the enthalpy change of **1d** is 39.1 KJ/mole, but that of **1b** is 229.2 KJ/mole. Azo dye **1b** possesses a mosaic texture under an optical polarizing microscope in the SmB phase and was further studied by powder XRD (Fig. 3). At 88 °C, two types of major reflection peaks are observed. One set of major reflection peaks are found at approx. 3.4° (stronger; 26.10 Å) and 13.4° (weaker; 6.61 Å), which result from the first-ordered and fourth-ordered reflection of the molecule **1b** along the z direction, respectively. The other set of major reflection peaks at approx. 10.0° (stronger, first-ordered; 8.83 Å) and 20.1° (weaker, second-ordered; 4.42 Å) together with other minor reflection peaks at approx. 10.8, 16.8, 22.6 and 23.5° should all result from the reflection of the molecule in hexagonal arrangement on the X-Y plane.

As indicated previously, the mesogenic behavior of liquid crystals may change according to the different lengths of the alkyl chain.^{4,5,7} To understand the length of alkyl chain on the influence of molecular packing in the solid state in the presence of other functional groups, azo dye **1d** was therefore studied by single crystal determination, and its molecular stacking was then established on the basis of the crystallographic data for comparison with those of azo

dyes **1a** and **1b** (Fig. 4). As the molecule **1d** is disordered in the solid state, some atoms are omitted for clarity on establishing the molecular stacking. Each molecule of **1d** is regularly arranged by a head-to-head or tail-to-tail pattern with its adjacent molecules in the same layer (e.g. mole-

cules a1 and a2 in the A layer) and found to be parallel to the neighboring molecules. The distances between corresponding atoms in the same layer (e.g. Na and Nb, Ca and Cb) are estimated to be approx. 5.98 Å, which are close to the corresponding distances (5.51 and 5.57 Å) found in azo

Fig. 2a. The DSC analysis of azo dye **1b**.

Fig. 2b. The texture of azo dye **1b** at 55 °C during the cooling process.

Fig. 3. The powder X-ray diffraction (XRD) pattern of compound **1b** at 88 °C.

Fig. 4. The molecular packing of compound **1d** in the solid state. The hydrogen atoms are omitted for clarity.

dyes **1a** and **1b**, respectively.⁵ The molecules in different layers are also similarly arranged with the adjacent molecules in different layers (e.g. molecules in the A and B layers in Fig. 4), which are different from the arrangements in the molecular stackings of azo dyes **1a** and **1b** (Figs. 5 and 6). For **1a** and **1b**, the molecules in different layers are approximately parallel to each other.⁵ In other words, the

quadrupolar interaction between benzene moieties is not significant (Figs. 5, 5a, 6, 6a). However, for azo dye **1d**, the quadrupolar interaction between benzene moieties, to some extent, influences the molecular stacking; the aryl-Hs in one molecule are directed to the plane containing benzene moiety in an adjacent molecule,⁵ and the intercepting angle between the plane containing azobenzene moiety of mole-

Fig. 4a. The molecular packing of compound **1d** in the solid state along the view of the z direction. The hydrogen atoms are omitted for clarity.

Fig. 5. The molecular packing of compound **1a** in the solid state. The hydrogen atoms are omitted for clarity.

Fig. 5a. The molecular packing of compound **1a** in the solid state along the view of the z direction. The hydrogen atoms are omitted for clarity.

cule a and the corresponding plane of molecule b is estimated to be about 40° based on crystallographic data (Fig. 4a).

It is believed that such an arrangement in the molecular stacking should also partly arise from the weak H-bond interaction in the molecular stacking. In Fig. 4a, the distances between O (CO_2) and aromatic C or saturated C pairs in adjacent layers are similar: Both $\text{C1}\cdots\text{O1}$ and $\text{C2}\cdots\text{O2}$ distances are $3.40 \text{ \AA}$ and also both $\text{C5}\cdots\text{O5}$ and $\text{C6}\cdots\text{O6}$ distances are $3.32 \text{ \AA}$. Consequently, the distances for $\text{H}(\text{at Cn})\cdots\text{On}$ ($n = 1, 2$) and $\text{H}(\text{at Cn})\cdots\text{On}$ ($n = 5, 6$) are short and which are calculated as 2.55 and $2.59 \text{ \AA}$, respectively; these distances are shorter than the sum of the van der Waals radii of H and O atoms (Bondi radii: H 1.20 , O 1.52).^{9a}

The H-bond interaction between the terminal ethoxy-carboxylate moieties of molecules in the same or adjacent layers also contributes in the molecular stacking: The $\text{C3}\cdots\text{O3}$ and $\text{C4}\cdots\text{O4}$ distances are both $3.78 \text{ \AA}$ and the $\text{C3}'\cdots\text{O3}'$ and $\text{C4}'\cdots\text{O4}'$ distances are both $3.62 \text{ \AA}$. Consequently, the distances for $\text{H}(\text{at Cn})\cdots\text{On}$ ($n = 3, 4$) and $\text{H}(\text{at$

$\text{Cn}')\cdots\text{On}'$ ($n = 3, 4$) are 3.00 and $2.83 \text{ \AA}$, respectively, which are slightly longer than the sum of the van der Waals radii of H and O atoms. It is noteworthy that the aromatic or saturated C–H in this case acts as the H-bond donor for the formation of the intermolecular H-bond with an O atom in the liquid crystalline network. Though unusual, this has been observed in other systems.^{5,9b-9e}

To understand the influence of the polarity of the CO_2 group, quadrupolar interaction and intermolecular H-bonding interaction on the conformation of the azo dye molecules in the solid state, the corresponding conformations of **1a**, **1b** and **1d** are established from crystallographic data, and the bond distances of Oa–Cy and Ha'–Ob' together with the dihedral angles of Oa–Cx–Ob–Cy and Ha'–Cx'–Cy'–Ob' for **1a**, **1b** and **1d** are respectively calculated (Table 2 and Fig. 7): The dihedral angles of Ha'–Cx'–Cy'–Ob' in compounds **1a**, **1b** and **1d** are calculated as 3.32 , 0.25 and 6.85° , respectively. The dihedral angles of Oa–Cx–Ob–Cy in compounds **1a**, **1b** and **1d**, which are calculated as 1.15 , 1.05 and 2.62° , also demonstrate a similar trend as those of Ha'–Cx'–Cy'–Ob'. It may thus be regarded that the mutual

Fig. 6. The molecular packing of compound **1b** in the solid state. The hydrogen atoms are omitted for clarity.

Fig. 6a. The molecular packing of compound **1b** in the solid state along the view of the z direction. The hydrogen atoms are omitted for clarity.

Table 2. Some of the distances of two atoms and dihedral angles for compounds **1a**, **1b** and **1d**

	Distance of Oa-Cy (Å)	Dihedral angle of Oa-Cx-Ob-Cy (°)	Distance of Ha'-Ob' (Å)	Dihedral angle of Ha'-Cx'-Cy'-Ob' (°)
compound 1a	2.69	1.15	2.38	3.32
(optimized)*	(2.63)	(0.49)	(2.57)	(4.87)
compound 1b	2.68	1.05	2.42	0.25
(optimized)*	(2.63)	(0.48)	(2.57)	(4.69)
compound 1d	2.70	2.62	2.50	6.85
(optimized)*	(2.59)	(0.15)	(2.56)	(4.53)

* The optimization was completed on the basis of original conformation from crystallographic data.

Table 3. Some of the intermolecular H-bond distances for compounds **1a**, **1b** and **1d**

	Distances (Å) of H (at C1)-O1 and H (at C2)-O2	Distances (Å) of H (at C3)-O3 and H (at C4)-O4	Distances (Å) of H (at C5)-O5 and H (at C6)-O6
compound 1a	2.85	2.75	2.57
compound 1b	3.02	3.00	2.58
compound 1d	2.55	3.00 (2.83*)	2.59

* Distances (Å) of H (at C3')-O3' and H (at C4')-O4'.

interaction in molecular stacking **1d** between adjacent layers (e.g. layers A and B in Figs. 4a, 5, 6) is strongest and the mutual interaction in molecular stacking **1b** is weakest among azo dyes **1a**, **1b** and **1d**. This result is also consistent with the intermolecular H-bond interaction in the molecu-

lar stackings of **1a**, **1b** and **1d** (Table 3). The H-bond distances of H(at Cn)⋯On (n = 1, 2), H(at Cn)⋯On (n = 5, 6) and H (at Cn')⋯On' (n = 3, 4) between adjacent layers in **1d** are calculated as 2.55, 2.59 and 2.83 Å, respectively. The H-bond distances of H (at Cn)⋯On (n = 1,2) and H(at

Fig. 7. The conformation of a single molecule for compounds **1a**, **1b** and **1d**.

Cn)···On ($n = 5, 6$) between adjacent layers in **1a** are calculated as 2.85, and 2.57 Å, respectively; analogously, the corresponding H-bond distances in **1b** are calculated as 3.02, and 2.58 Å, respectively.

The conformations of azo dyes **1a**, **1b** and **1d** were further optimized by the CaChe program, using the AM1 model in the gas phases. After optimization, the bond distances of Oa-Cy and Ha'-Ob' together with the dihedral angles of Oa-Cx-Ob-Cy and Ha'-Cx'-Cy'-Ob' for **1a**, **1b** and **1d** are further calculated (Table 2 and Fig. 7). The corresponding bond distances and dihedral angles are not significantly different. This indicates that in the gas phase, the conformation of molecules **1a**, **1b** and **1d** might be quite similar because of the absence of the polar attraction and quadrupolar and intermolecular H-bonding interaction. However, the conformations of molecules **1a**, **1b** and **1d** in the solid state are different because of these forces in the corresponding molecular stackings.

Additionally, it is worthwhile to discuss the H-bond interaction between different molecules in the same layer for **1a**, **1b** and **1d**: The H-bond distances of H(at Cn)···On ($n = 3, 4$) in **1a** are calculated as 2.75 Å, and those of corresponding distances are both 3.00 Å for **1b** and **1d**. The stronger interaction between two ending functional groups in **1a** may lead to the bending of the molecular stacking as shown in Fig. 5a and the resulting nematic phase is thus observed. It is known that liquid crystal with SmA phase possesses a layer structure; additionally, if a regular hexagonal arrangement exists among the layer structure, then a SmB phase is expected. Based on the above observations, it is clear that the interactions between adjacent layers are stronger in **1d** than those in **1b**. This stronger interaction in some regional areas leads to the breaking of regular hexagonal arrangement, and thus azo dye **1b** shows a SmB phase but **1d** shows a SmA phase during the thermal process.

In summary, we have clearly showed that azo dyes **1a**, **1b** and **1d**, having the same core and different lengths of alkyl chains, possess various mesogenic behaviours and their corresponding molecular stackings are different based on crystallographic study.¹⁰ Although we do not directly demonstrate the exact molecular arrangements of **1a**, **1b** and **1d** in the liquid crystalline phases, we do show that different lengths of alkyl chain obviously can lead to the various stackings of **1a**, **1b** and **1d** in the solid state because of the different interaction of functional polarity, H-bond and

quadrupolarity of benzene moiety.

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