

N,N-Disubstituted aminophenylazo-4-benzoates: preparation, mesogenic study, structure determination and molecular modelling

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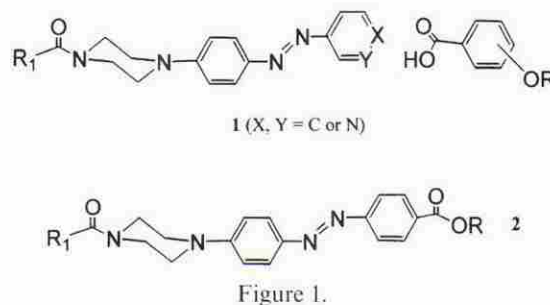
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A series of alkyl *N,N*-disubstituted aminophenylazo-4-benzoates were prepared from the reactions of an acyl phenylpiperazine with a series of the diazonium salts. The mesogenic behaviours of the resulting dyes were studied by polarizing optical microscopy and differential scanning calorimetry. Single crystal structure determination, powder XRD, and molecular modelling of a representative compound were also undertaken to understand the relative structural conformation.

1. Introduction

Azo dye molecules are attracting much attention in both academic and applications areas [1, 2]. In particular, azo-dyes have a reasonable dichroic ratio and are suitable for low power consumption reflective liquid crystal (LC) devices; the three-layered guest–host (G–H) systems are expected to be used for developing full colour reflective displays [3]. In these systems, the yellow, magenta, and cyan dyes are, respectively, incorporated into different liquid crystal cells. However, the dye solubility and the phase transition temperatures of the G–H systems are serious issues in applications studies. The clearing temperatures usually vary with the components of the G–H systems, and addition of the non-mesogenic dyes often causes instability of the corresponding LC phases [4]. Dyes which are themselves mesogenic minimize this effect; therefore azo dye liquid crystals are therefore highly desirable as dopants.

In previous work [5], we reported mesogenic studies on the azo dye derivatives **1** and **2** as shown in figure 1. We found that all the molecules showed smectic C phases, and that the mesogenic range seemed unrelated to the alkoxy chain length of the benzoate in the hydrogen bonded system **1**, or to the chain length of the

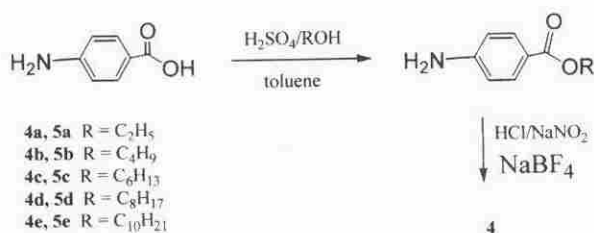
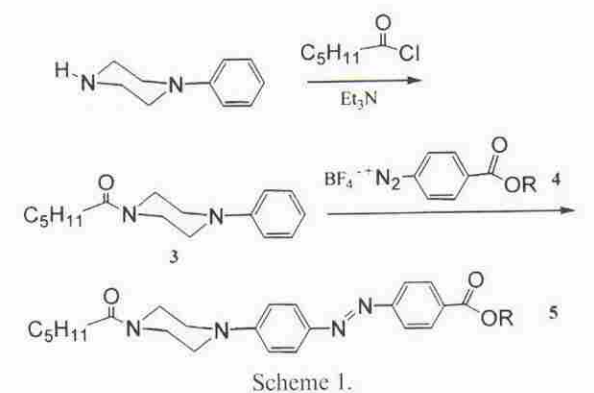


carboxylate in compound **2**. This differs from our former observations in the quinoline system [6], in which the length of the alkoxy chain does affect the range of the smectic C phase. For a better understanding of these molecules, we have further synthesized compounds **5a–5e** (schemes 1 and 2), as these SmC phase-exhibiting materials have potential for ferroelectric or antiferroelectric devices. Compound **5b**, representatives of this series of molecules, was studied by single crystal structure determination, powder X-ray diffraction (XRD) and molecular modelling.

2. Experimental

The chemicals used in this work were commercially available from ACROS. High resolution mass spectra were obtained by a VG70-250S spectrometer (EI, 70 ev),

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- 4a, 5a R = C₇H₅
 4b, 5b R = C₈H₉
 4c, 5c R = C₆H₁₃
 4d, 5d R = C₈H₁₇
 4e, 5e R = C₁₀H₂₁

and ¹H NMR spectra were recorded on a Varian 200 FT NMR spectrometer. The mesogenic behaviours and phase transitions were characterized by polarizing optical microscopy (POM) and differential scanning calorimetry (Perkin-Elmer DSC 6). XRD patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK 450 temperature controller and a Cu radiation with the wavelength $\lambda = 1.5406 \text{ \AA}$. Semi-empirical calculation was carried out by the CACHE program, provided by Fujitsu (Japan). The structure of the molecule **5b** was optimized by performing a geometry calculation in mechanics using augmented MM3 parameters, and further refined by calculating the optimized geometry by MOPAC using PM3 parameters.

2.1. Synthesis of the alkyl *N,N*-disubstituted aminophenylazo-4-benzoates **5**

N-Phenylpiperazine (8.05 g, 50 mmol) was dissolved in dry dichloromethane (100 ml). Dry triethylamine (10 ml), followed by hexanoyl chloride (6.73 g, 50 mmol) was then added at 0–5 °C. The resulting solution was further stirred at room temperature for 30 min. NaOH (3 g) in water (50 ml) was added, and the solution was extracted with dichloromethane (50 ml). The combined extracts were dried over sodium sulphate and the solvent was removed under reduced pressure. Hexane (20 ml) was added to give *N*-hexanoyl-*N'*-phenylpiperazine **3** in an almost quantitative yield.

The phenylpiperazine derivative **3** (1.3 g, 2 mmol) and the corresponding diazonium salts **4** [7] (2.5 mmol) were added to a solution of acetic acid/water (15 ml, 2:1),

and the solution was stirred at room temperature for 24 h. Water (100 ml) was added and the precipitated solid, was filtered off, washed with acetone (5 ml) and dried. The azo dyes **5**, after purification by chromatography for further physical study, were obtained in 50–70% yields. Products **5a–5d** were identified as the required materials and judged to be pure by ¹H NMR and high resolution mass spectroscopy. The following abbreviations and NMR spectra data are as follows: s=singlet, d=doublet, t=triplet, b=broad, *J*=coupling constant.

5a. ¹H NMR: δ (CDCl₃) 0.89 (t, 3H, CH₃), 1.29–1.78 (m, 9H, 3CH₂ + CH₃), 2.36 (t, 2H, CH₂), 3.38 (s, b, 4H, 2CH₂), 3.65 (t, 2H, CH₂), 3.79 (t, 2H, CH₂), 4.38 (quart, 2H, OCH₂), 6.96 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 7.87 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H), 7.91 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 8.14 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H). HRMS for C₂₅H₃₂N₄O₃ 436.2474; found 436.2476.

5b. ¹H NMR: δ (CDCl₃) 0.89 (t, 3H, CH₃), 1.03 (t, 3H, CH₃), 1.41–1.84 (m, 10H, 5CH₂), 2.36 (t, 2H, CH₂), 3.38 (s, b, 4H, 2CH₂), 3.65 (t, 2H, CH₂), 3.80 (t, 2H, CH₂), 4.33 (t, 2H, OCH₂), 6.96 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 7.86 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H), 7.91 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 8.14 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H). HRMS for C₂₇H₃₆N₄O₃ 464.2787; found 464.2787.

5c. ¹H NMR: δ (CDCl₃) 0.86–0.94 (m, 6H, 2CH₃), 1.30–1.92 (m, 14H, 7CH₂), 2.36 (t, 2H, CH₂), 3.38 (s, b, 4H, 2CH₂), 3.66 (t, 2H, CH₂), 3.80 (t, 2H, CH₂), 4.32 (t, 2H, OCH₂), 6.96 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 7.87 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H), 7.91 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 8.14 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H). HRMS for C₂₉H₄₀N₄O₃ 492.3100; found 492.3102.

5d. ¹H NMR: δ (CDCl₃) 0.85–0.92 (m, 6H, 2CH₃), 1.23–1.82 (m, 18H, 9CH₂), 2.36 (t, 2H, CH₂), 3.38 (t, 4H, 2CH₂), 3.65 (t, 2H, CH₂), 3.79 (t, 2H, CH₂), 4.32 (t, 2H, OCH₂), 6.96 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 7.86 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H), 7.91 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 8.14 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H). HRMS for C₃₁H₄₄N₄O₃ 520.3413; found 520.3411.

5e. ¹H NMR: δ (CDCl₃) 0.83–0.92 (m, 6H, 2CH₃), 1.22–1.82 (m, 22H, 11CH₂), 2.36 (t, 2H, CH₂), 3.38 (s, b, 4H, 2CH₂), 3.65 (t, 2H, CH₂), 3.80 (t, 2H, CH₂), 4.32 (t, 2H, OCH₂), 6.96 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 7.87 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H), 7.91 (d, 2H, *J* = 9.3 Hz, 2 × Ar-H), 8.14 (d, 2H, *J* = 8.4 Hz, 2 × Ar-H). HRMS for C₃₃H₄₈N₄O₃ 548.3726; found 548.3727.

2.2. X-ray crystallographic analysis

Crystals of compound **5b** were grown from dichloromethane/hexane (1:1) at room temperature. A single crystal of suitable quality was mounted on a glass fibre and used for the measurement of precise cell constants and intensity data collection. Diffraction measurements

were made on a Siemens SMART 1K CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), operated at room temperature over the θ range 0.70–26.36°. No significant decay was observed during the data collection. A total of 6652 reflections were collected, yielding 4880 unique reflections; 3442 reflections were observed with $I \geq 2\sigma(I)$ reflections. Data were processed on a PC using the SHELXTL software package [8]. Systematic absences in the diffraction data of **5b** established the space group as $P2_1$. The structure of **5b** was solved using direct methods and refined by full-matrix least square on F^2 value. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed at calculated positions and refined using a riding model. The final indices were $R1 = 0.0657$, $wR2 = 0.1347$ with goodness-of-fit = 1.075. The crystal data are summarized in table 1; selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. Synthesis and mesogenic study

The desired azo dye molecules **5a–5e** were synthesized as demonstrated in scheme 1. Compound **3** was obtained by reaction of *N*-phenylpiperazine with hexanoyl chloride in an almost quantitative yield. The diazonium salts **4a–4e** were prepared according to literature methods as described in scheme 2 [7]. The esterification process [9] gave about 60% yields, and the diazotisation was carried out in an almost quantitative yield. The mesogenic behaviours and phase transitions, characterized by POM and DSC are summarized in table 3. The smectic C phase appears during heating or cooling of the azo dye molecules; the mesogenic ranges are similar

Table 1. Crystallographic data for compound **5b**.

Formula	C ₂₇ H ₃₆ N ₄ O ₃
Formula weight	464.60
Space group	$P2_1$
$a/\text{\AA}$	5.8933(2)
$b/\text{\AA}$	7.6031(3)
$c/\text{\AA}$	29.1309(9)
β	92.826(1)°
$v/\text{\AA}^3$	1303.69(8)
Z	2
$D_c/\text{g cm}^{-3}$	1.184
μ/cm^{-1}	0.78
$2\theta_{\text{max}}/\text{deg}$	52.72
Reflns measd	6652
Reflns used (R_{int})	4880(0.0286)
Final R [$I > 2\sigma(I)$]	$R1^a = 0.0657$, $wR2^b = 0.1347$
R (all data)	$r1 = 0.0930$, $wr2 = 0.1601$
Goodness-of-fit on F^2	1.075

$$^a R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR2 = \left[\frac{\sum w[(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right]^{1/2}; w = 1/[\sigma^2(F_o^2) + (0.08P)^2], \text{ where } P = [\max(F_o^2, 0) + 2F_c^2]/3.$$

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for compound **5b**.

<i>Bond lengths</i>			
C1–C2	1.395(4)	C1–C6	1.401(4)
C1–N1	1.434(4)	C2–C3	1.383(4)
C3–C4	1.402(4)	C4–C5	1.400(4)
C4–C17	1.499(4)	C5–C6	1.383(4)
C7–C8	1.393(4)	C7–C12	1.400(4)
C7–N2	1.416(4)	C8–C9	1.386(4)
C9–C10	1.406(4)	C10–C11	1.416(4)
N1–N2	1.258(3)	O2–C18	1.469(3)
N2–C7	1.416(4)	O3–C22	1.233(4)
N3–C10	1.415(4)	N3–C13	1.467(4)
N3–C15	1.471(4)	N4–C22	1.360(4)
N4–C16	1.462(4)	N4–C14	1.465(4)
O1–C17	1.206(4)	O2–C17	1.346(4)
<i>Bond angles</i>			
C2–C1–N1	115.4(3)	C6–C1–N1	125.1(3)
C8–C7–N2	117.7(3)	C12–C7–N2	124.4(3)
O3–C22–N4	120.6(3)	O3–C22–C23	121.5(3)
N4–C22–C23	117.9(3)	N2–N1–C1	115.0(2)
N1–N2–C7	114.4(2)	C22–N4–C16	126.6(3)
C22–N4–C14	121.5(2)	C16–N4–C14	111.7(2)
C17–O2–C18	116.0(2)		

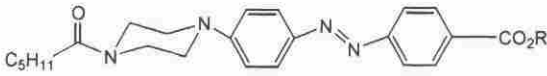
for either process (about 60–80°). The tilted SmC phase was characterized by the broken focal-conic fan texture coexisting with the schlieren texture. It was also confirmed by the XRD study. For example, d -spacings (the Z component of an extended molecular length) for compound **5b** are 28.16, 26.95, 26.73 and 26.69 \AA at 200, 180, 160 and 150°C, respectively. In the SmC range, the tilt angle between the molecular and the Z axis decreases with increasing temperature, and the d -spacing thus becomes greater at the higher temperature.

In previous work, we showed that nitrogen-containing heterocycles favour the formation of the SmC phase in LCS. Also, the chain length of the flexible part, which is related to the molecular stacking shape rather than the dipole moment, is important in enhancing the heterocyclic influence (to form an SmC phase with wider temperature range) [6]. However our present work shows that the chain length of the flexible carboxylate may not have a significant influence on widening the SmC phase. The C(=O)–N< moiety, introducing a strong dipole into the molecule, may be dominant in this case. Thus the chain length of the carboxylate moiety may have little effect on the molecular stacking.

3.2. Structural determination and molecular modelling

The structure of compound **5b** is shown in figure 2. The angles between plane C1–N2–N2–C7 and the two benzene rings (C1–C6 and C7–C12) are 6.73° and 6.87°, respectively. The rigid part of the molecule is almost planar. However, owing to the strong delocalization

Table 3. Phase transition temperature ($^{\circ}\text{C}$) and corresponding enthalpies (J g^{-1}), in parentheses, of azo dyes **5**. The phase transition temperatures and corresponding enthalpies of **5** were determined by the 2nd DSC scans using Perkin Elmer DSC-6 at heating and cooling rates of $10^{\circ}\text{C min}^{-1}$ between 45 and 240°C . Cr = crystalline; SmX = unidentified smectic phase, SmX' = unidentified smectic phase, SmC = smectic C phase, I = isotropic liquid.



5

5a		$\text{Cr} \rightleftharpoons$	$\begin{matrix} 115.7(15.0) \\ 65.7(3.4) \end{matrix}$	$\text{SmX} \rightleftharpoons$	$\begin{matrix} 149.4(0.3) \\ 131.0(0.7) \end{matrix}$	$\text{SmC} \rightleftharpoons$	$\begin{matrix} 217.7(7.9) \\ 213.0(7.1) \end{matrix}$	I
5b	$\text{Cr} \xrightarrow{134.0}$	$\text{SmX}' \rightleftharpoons$	$\begin{matrix} 69.3(1.5) \\ 136.7^{\text{a}} \end{matrix}$	$\text{SmX} \rightleftharpoons$	$\begin{matrix} 135.0(0.5) \\ 132.3(1.8) \end{matrix}$	$\text{SmC} \rightleftharpoons$	$\begin{matrix} 207.4(10.5) \\ 201.3(7.3) \end{matrix}$	I
5c	$\text{Cr} \xrightarrow{101.7(60.0)}$	$\text{SmX}' \rightleftharpoons$	$\begin{matrix} 117.4(1.4) \\ 75.7(3.4) \end{matrix}$	$\text{SmX} \rightleftharpoons$	$\begin{matrix} 134.1(2.4) \\ 132.3(1.8) \end{matrix}$	$\text{SmC} \rightleftharpoons$	$\begin{matrix} 203.4(22.9) \\ 201.6(20.8) \end{matrix}$	I
5d	$\text{Cr} \xrightarrow{100.7(43.5)}$	$\text{SmX}' \rightleftharpoons$	$\begin{matrix} 109.0(5.2) \\ 78.6(11.4) \end{matrix}$	$\text{SmX} \rightleftharpoons$	$\begin{matrix} 132.7(1.6) \\ 134.6(1.3) \end{matrix}$	$\text{SmC} \rightleftharpoons$	$\begin{matrix} 200.4(18.9) \\ 198.0(16.7) \end{matrix}$	I
5e	$\text{Cr} \xrightarrow{91.7(42.5)}$	$\text{SmX}' \rightleftharpoons$	$\begin{matrix} 78.6(10.1) \\ 132.4(2.7) \end{matrix}$	$\text{SmX} \rightleftharpoons$	$\begin{matrix} 130.6(1.8) \\ 132.4(2.7) \end{matrix}$	$\text{SmC} \rightleftharpoons$	$\begin{matrix} 197.4(19.1) \\ 195.6(17.0) \end{matrix}$	I

^aThe peaks are overlapped and the total enthalpy is 18.3 J g^{-1} .

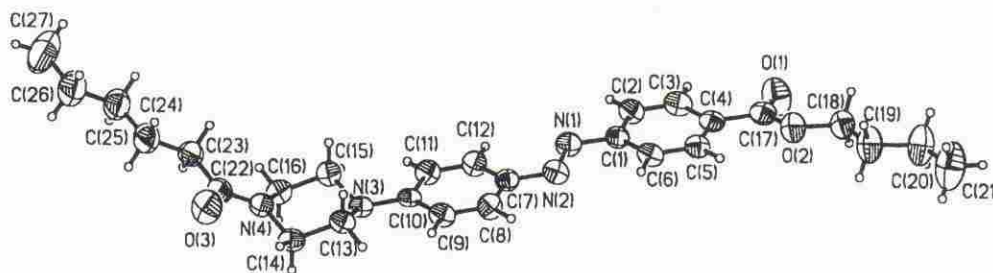


Figure 2. The molecular structure of compound **5b**, thermal ellipsoids drawn at the 50% probability level.

of the $\text{C}(=\text{O})\text{-N}<$ moiety itself, there is considerable bending between the piperazine and the acyl chain as shown in figure 3. On the basis of the crystallographic structure, the distance between C21 and C27 is 26.09 \AA , which is quite close to the d -spacing from the XRD study 26.95 \AA at 90°C (smectic X phase) and 170°C (smectic C phase).

The packing diagram for the intermolecular interaction of compound **5b** in the solid state is shown in figure 4. Compound **5b** is arranged in the head-to-tail

position, i.e. the carboxylate end is directed toward the piperazine end; W-shaped packing is thus formed. The adjacent layers of the molecules are also arranged head-to-tail, but in the opposite direction, which may result from the influence of the piperazine unit. In such a packing, the congestion from two piperazine moieties can be avoided. From the literatures [10], we find that the N -substituents of the piperazine favour the equatorial conformation, and that the energy barrier between the equatorial and axial conformation is only $1.9\text{--}4 \text{ kcal mol}^{-1}$.

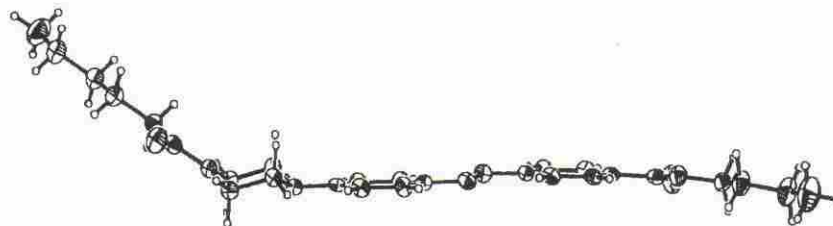


Figure 3. Horizontal view of compound **5b**.

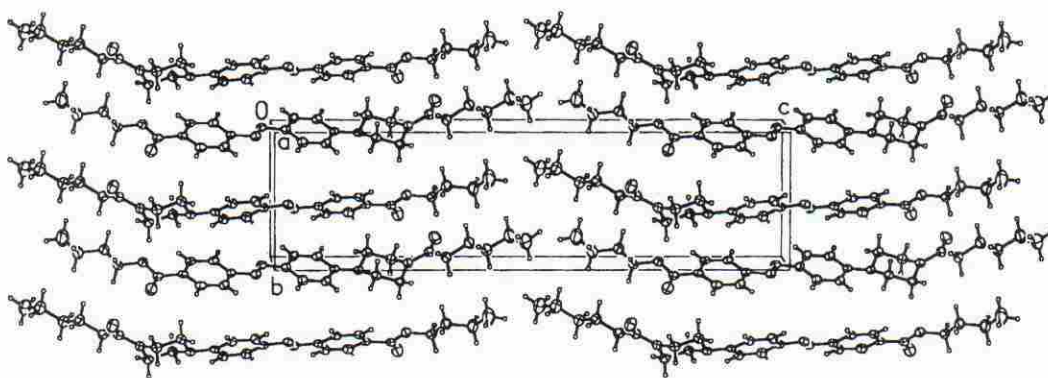


Figure 4. Packing diagram showing the intermolecular interaction of compound **5b** in the solid state.

Compound **5b** was also studied in more detail by semi-empirical calculation using the CAChe program. The structure of molecule **5b** was optimized by performing a geometry calculation in mechanics using augmented MM3 parameters and further refined by calculating the optimized geometry by MOPAC using PM3 parameters. After optimization, the length of molecule **5b** is 26.10 Å, in which the C=O moiety is directed in the equatorial position and the corresponding heat of formation is $-66.13 \text{ kcal mol}^{-1}$ (figure 5). If the C=O functional group is directed in axial position as in figures 6(a) or 6(b), the molecular lengths are 25.62 and 26.38 Å, respectively, and the corresponding heats of formation are -66.10 and $-65.01 \text{ kcal mol}^{-1}$. It seems there is no energy barrier between the figure 5 and figure 6(a)

structures, and the energy barrier between the figures 5 and 6(a) conformation and the figure 6(b) conformation is about $1.10 \text{ kcal mol}^{-1}$, which is also small and consistent with literature values. We may therefore conclude that vibration of the $>\text{N}-\text{C}=\text{O}$ group of compounds **5** in the mesogenic range likely happens, and that the conformation in figures 5 and 6(b) may also exist, being more linear and favouring the formation of the LC phase.

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Figure 5. The optimized structure **5b** by CAChe program, in which the C=O group is at the equatorial position of the piperazine moiety. The corresponding heat of formation is -66.13 Kcal/mol and the distance of two ending carbons is 26.10 Å.

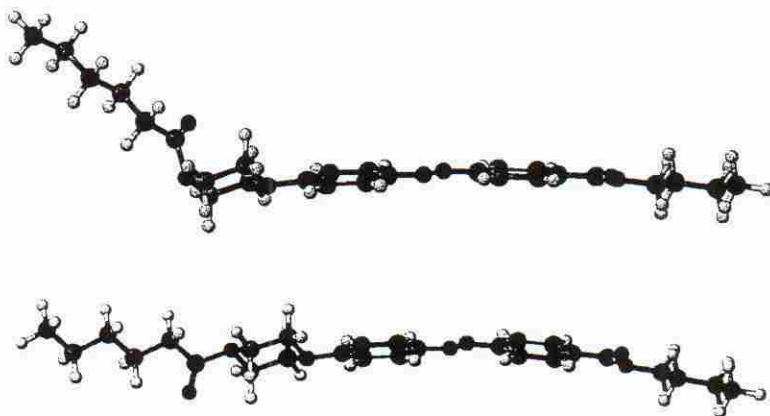


Figure 6. (a) The optimized structure **5b** by CAChe program, in which the C=O group is at the axial position of the piperazine moiety. The corresponding heat of formation is -66.10 Kcal/mol and the distance of two ending carbons is 25.62 Å. (b) The optimized structure **5b** by CAChe program, in which the C=O group is at the axial position of the piperazine moiety. The corresponding heat of formation is -65.01 Kcal/mol and the distance of two ending carbons is 26.38 Å.

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