# Non-Symmetric Liquid Crystal Dimers Containing Azobenzene and 1,3,4-Oxadiazole Group: Synthesis and Mesomorphic Behaviour

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**Abstract:** We report on the synthesis and mesomorphic behaviour of a new series of non-symmetric liquid crystal dimers with long terminal chains containing 1,3,4-oxadiazole group and azobenzene group as the mesogenic units. These non-symmetric liquid crystal dimers are evidenced to display monolayer smectic A phase. Microphase segregation and specific intermolecular interactions between the two different mesogenic units are the major driving forces for the formation of the monolayer smectic A structure.

**Keywords:** Azobenzene, intercalated structure, interdigitated structure, liquid crystal dimers, 1,3,4-oxadiazole, non-symmetric dimers, symmetric dimers.

## 1. INTRODUCTION

Liquid crystal dimers, which contain either two identical (symmetric) or non-identical (non-symmetric) mesogenic units connected *via* a flexible central spacer [1], have attracted increasing attention because not only they are regarded as model compounds for polymeric liquid crystals, but also they are of significant interest in their own right and exhibit quite different behaviour to conventional low molar mass mesogens, such as their novel molecular architecture, unique phase behaviours and mesophase polymorphism etc. [2-4].

There are remarkable differences in the behaviour of non-symmetric and symmetric dimers. As has been reported, symmetric dimers containing terminal alkyl chains appear to have a strong tendency to exhibit monolayer smectic phases, the driving force for which is thought to be the incompatibility between the terminal alkyl chains and the spacers, leading to a microphase separation into three regions: terminal chains, mesogenic groups and flexible alkyl spacers [1]. In contrast, the example of non-symmetric liquid crystal dimers exhibiting monolayer smectic phases is rarely [5]. Usually, non-symmetric liquid crystal dimers exhibit intercalated smectic phases, in which specific intermolecular interactions between the two different mesogenic units are responsible for this specific phase behavior [1, 6].

In our previous work, it has been demonstrated that non-symmetric liquid crystal dimers, 1-[4-(4’-methoxyphenylazo)phenoxyl]-m- [(N-(4- alkoxybenzoyl) -N’-(benzoyl-4’-oxy)hydrazine)] alkane (**EmCn**) (see Scheme **1**, where m signifies the number of methylene units in the spacer and n indicates the length of terminal alkoxy tail) with long terminal chains exhibit a monolayer smectic C phase, for which intermolecular hydrogen bonding between hydrazide groups is considered to be the main driving forces [7]. So, in order to validate the importance of intermolecular hydrogen bonding between hydrazide groups in formation of monolayer smectic phase, we have prepared non-symmetric dimers containing azobenzene and 1,3,4-oxadiazole group with long terminal alkoxy chains, i.e. 1-[4-(4’-methoxyphenylazo)phenoxyl]-m- [(N-(4- cetyloxybenzoyl) -N’-(benzoyl-4’-oxy) 1,3,4-oxadiazole] alkyl (**EmC16-OXD**, Scheme **1**). Interestingly, the compound **E6C16-OXD**, non-symmetric liquid crystal dimer with long terminal chains, exhibits a monolayer smectic A phase.

## 2. EXPERIMENTAL

### 2.1. Synthesis

The target non-symmetric dimers, abbreviated as **EmC16-OXD** (where m <m=5, 6> signifies the number of methylene units in the spacer), were synthesized through the route shown in Scheme **1**. The chemical structures of the resulting compounds were confirmed by FT-IR, $^1$H NMR spectroscopy and elemental analysis (Because of the poor solubility, $^1$H NMR experiment of **E6C16-OXD** was not performed.).

Synthesis of 1-[4-(4’-methoxyphenylazo)phenoxyl]-5-[(*N*-(4- cetyloxybenzoyl) -*N*’-(benzoyl-4’-oxy)-1,3,4-oxadiazolyl)] pentane (**E5C16-OXD**) (see Scheme **1**).

1-[4-(4’-methoxyphenylazo)phenoxyl]-5- [(*N*-(4- cetyloxybenzoyl) -*N*’-(benzoyl-4’-oxy)hydrazine)] pentane (**E5C16**) (1.50 g, 1.89 mmol) was added into 70 mL phosphorous oxychloride ($POCl_3$) and refluxed for about 24 h. After cooling to room temperature, the mixture was poured into water. And the precipitate was filtered, washed

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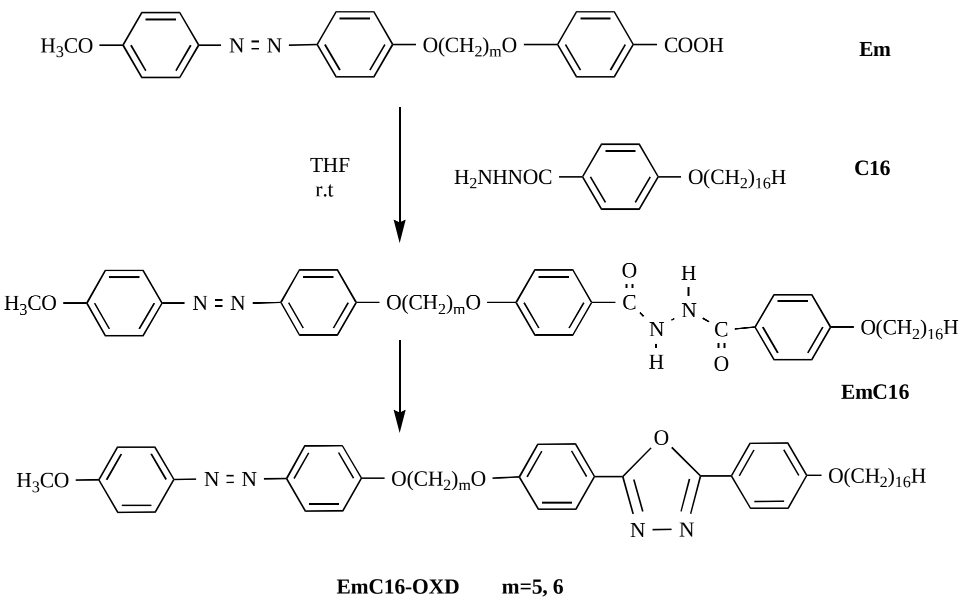


**Scheme 1.** The synthetic routes for EmC16-OXD.

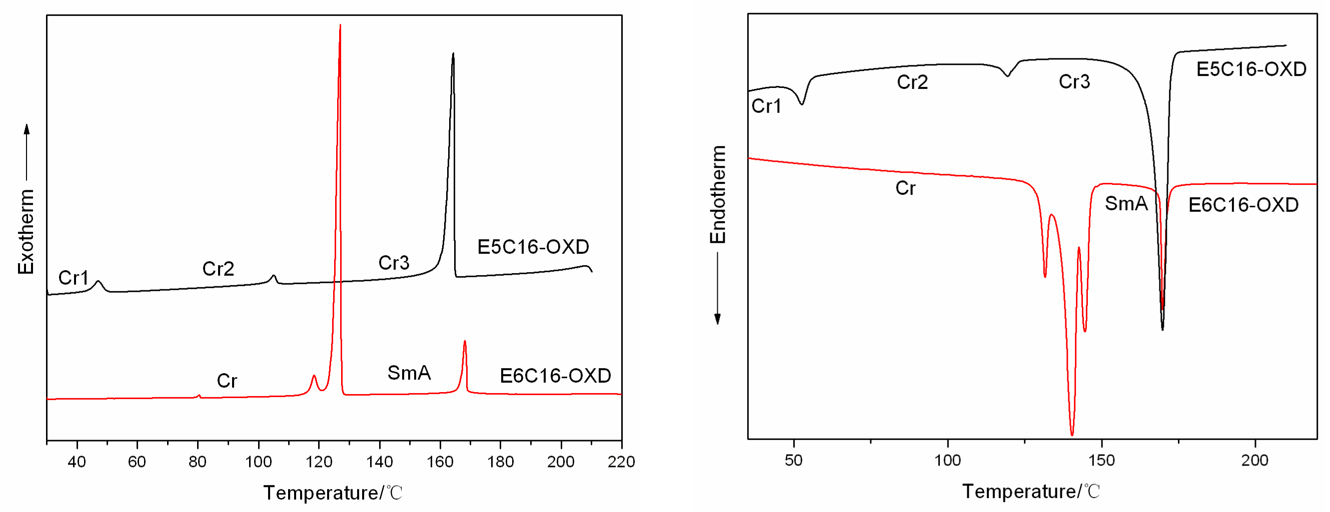
thoroughly with water, dried completely, and recrystallized from DMF.

1H NMR (300 MHz, $CDCl_3$), (ppm, from TMS): 8.05 (dd, *J* = 8.97, 2.45 Hz, 2H), 7.92 (dd, *J* = 9.05, 1.46 Hz, 1.8H), 7.60 (s, 0.2H), 7.04-6.99 (m, 3.7H), 6.91-6.86 (m, 0.3H), 4.12-4.01 (m, 6H), 3.88 (d, *J* = 6.50 Hz, 3H), 1.95-1.26 (m, 30H), 0.88 (t, *J* = 6.75 Hz, 3H). FTIR (KBr, pellet, $cm^{-1}$): 2921, 2851, 1612, 1603, 1582, 1497, 1472, 1396, 1251, 1176, 1145, 1104, 1035, 835, 743, 676. Elem. Anal: Found: C74.31, N7.21, H8.06; Calcd for $C_{48}H_{62}N_4O_5$: C74.39, N7.23, H8.06.

Using the same method, compound **E6C16-OXD** was successfully synthesized and characterized. FTIR (KBr, pellet, $cm^{-1}$): 2918, 2849, 1616, 1603, 1583, 1497, 1473, 1465, 1396, 1249, 1176, 1152, 1103, 1026, 843, 744, 674. Elem. Anal: Found: C74.39, N7.12, H8.40; Calcd for $C_{49}H_{64}N_4O_5$: C74.59, N7.10, H8.18.

## 2.2. Characterization

$^1$H NMR spectra were recorded with a Mercury-300BB 300 MHz spectrometer, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded with a Perkin–Elmer spectrometer (Spectrum One B) using KBr pellets. The thermal properties of the compounds were investigated with a Mettler-Toledo DSC821$^e$ instrument. The rate of heating and cooling was 10℃$min^{-1}$; the weight of the sample was about 2 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. Optical textures were observed by polarizing optical



(**a**) (**b**)

**Fig. (1).** DSC curves of **E5C16-OXD** and **E6C16-OXD** (**a**) on the first cooling run and (**b**) on the second heating run.

**Table 1. Transition Temperatures（℃）and Enthalpies (kJ $mol^{-1}$, in Parentheses) of EmC16-OXD**

| Compds | First cooling | Second heating |
|---|---|---|
| **E5C16-OXD** | I 164 (56.3) Cr3 105 (2.3) Cr2 47 (4.4) Cr1 | Cr1 53 (4.3) Cr2 120 (2.9) Cr3 170 (57.6) I |
| **E6C16-OXD** | I 168 (6.8) SmA 127 (52.1) Cr 118 (2.8) Cr | Cr 132 (8.8) Cr 140 (37.1)Cr 145 (11.8) SmA 170 (7.3) I |
| **E5C16** | I 169 (8.4) SmC 147 (36.9) Cr 116 (1.2) Cr | Cr 119 (1.0) Cr 141 (20.0) Cr 170 (47.7) I |
| **E6C16** | I 199 (14.6) SmC 177 (42.7) Cr 156 (16.7) Cr | Cr 188 (74.6) SmC 201(14.1) I |

Cr, SmA, SmC and I indicate crystalline state, smectic A, smectic C phase and isotropic liquid, respectively. The rate of heating and cooling was 10℃$min^{-1}$.

microscopy (POM) using a Leica DMLP microscope equipped with a Leitz 350 heating stage. X-ray diffraction was carried out with a Bruker Avance D8 X-ray diffractometer.

## 3. RESULTS AND DISCUSSION

The phase behavior of **E5C16-OXD** and **E6C16-OXD** were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and powder XRD. Fig (**1**) shows the DSC thermograms of **E5C16-OXD** and **E6C16-OXD** on the first cooling and on the second heating run at a scanning rate of 10 ℃/min. The phase transitional temperatures and the associated enthalpic changes for **E5C16-OXD** and **E6C16-OXD** are summarized in Table **1**. It can be seen that spacer plays an important role in the formation of the mesophase. **E6C16-OXD** shows enantiotropic liquid crystalline behaviours, whereas **E5C16-OXD** is non-mesomorphic. And because of the higher melting point suppressing the LC phase for **E5C16-OXD**, the characteristic odd–even effect, as usually observed in liquid crystal dimers, is not observed. This phenomenon is in accordance with the results of the **Ep-m-$NO_2$** systems reported previously by us [8]. The polarizing optical photomicrograph of compound **E6C16-OXD** is shown in Fig. (**2**), and no schlieren texture is observed on shearing.

**Fig. (2).** Polarizing optical photomicrograph of **E6C16-OXD** at 152 ℃ (×200).

In order to obtain further information on molecular arrangements in their mesophase, variable temperature XRD was performed. The XRD pattern of **E6C16-OXD** in the smectic phase contains two sharp peaks in the low angle region implying the formation of a layered structure, and a broad diffuse peak in the wide angle region centered at a spacing of 4.6Å, indicating liquid-like arrangement of the molecules within the layers, as shown in Fig. (**3**). The layer spacing (d) of **E6C16-OXD** is 59.49 Å, which is a little bit longer than the estimated all-trans molecular length (*l*) of the most extended conformation of 56.07 Å, considering its texture in mesophase, indicating that the molecules of **E6C16-OXD** are arranged in a monolayer arrangement with the molecular long axis perpendicular with respect to the layer normal (SmA).

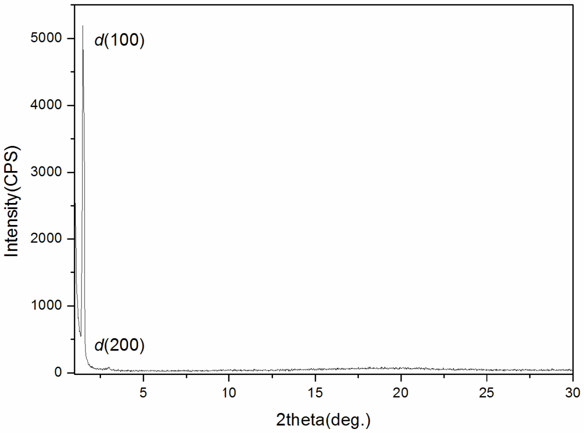


**Fig. (3).** XRD pattern of **E6C16-OXD** at 160℃ on first cooling run.

We have reported previously that non-symmetric liquid crystal dimers (**EmC16**, Scheme **1**) with long terminal chains exhibit a monolayer smectic C phase, for which the intermolecular hydrogen bonding between hydrazide groups is considered to be the main driving forces. In contrast, for **E6C16-OXD**, 1,3,4-oxadiazole group replacing the dihydrazide group of **E6C16**, no hydrogen bonding interactions existed in mesophase. We found that both the melting and clearing points of **E6C16-OXD** are much lower than those of **E6C16**, and the enthalpy change of clearing point transition of **E6C16-OXD** was two times lower than that of the **E6C16**, and **E6C16-OXD** exhibits a monolayer smectic A phase. It is confirmed that the lateral hydrogen bond between the dihydrazide groups indeed plays an important role for the formation of mesophases for **E6C16**, but it is not the exclusively factor for the formation of monolayer smectic structure. And the terminal groups and spacers must also be important.

For **E6C16-OXD**, the terminal chain length is farther greater than the spacer length, the incompatibility between the long terminal alkyl chains and the spacers does not approve the intercalated structure. And the terminal nonpolar methoxyl group does not approve the interdigitated structure usually stabilized by the electrostatic interaction between the polar groups such as cyanobiphenyl groups, nitryl groups etc. [6a, 6b] in non-symmetric liquid crystal dimers with long terminal alkyl chains. Thus the **E6C16-OXD** exhibits a monolayer smectic A phase and we propose that the structure of monolayer SmA phase of **E6C16-OXD** should be as shown in Fig. (**4**) [1c, 5a], the driving force for which is thought to be specific intermolecular interactions between the two different mesogenic units and the incompatibility between the long terminal alkyl chains and the spacers, leading to a microphase separation into three regions: the long terminal alkyl chains, mesogenic groups and flexible alkyl spacers.

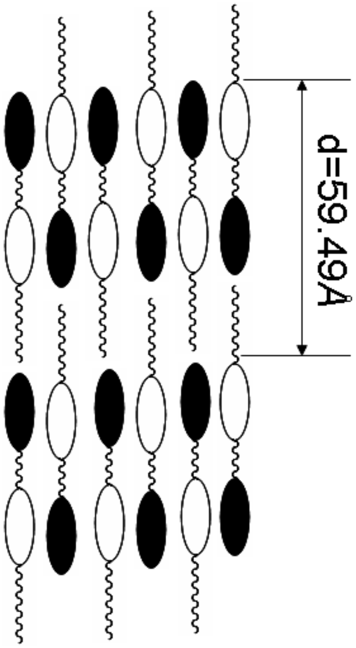


**Fig. (4).** A sketch of the monolayer smectic A of **E6C16-OXD** (filled ellipse represents azobenzene mesogenic groups and unfilled ellipse represents 1,3,4-oxadiazole mesogenic groups).

## 4. CONCLUSION

In conclusion, non-symmetric liquid crystal dimers with long terminal chains, containing a 1,3,4-oxadiazole group and an azobenzene group as the mesogenic units have been designed and smectic A phase observed in these non-symmetric dimers. Microphase segregation and specific intermolecular interactions between the two different mesogenic units are the major driving forces for the formation of the monolayer smectic A structure. Both the terminal groups and the flexible spacers play key roles in the formation of the stable smectic phase.

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## DISCLOSURE

The part of information about compound EmCn included in this article has been previously published in Journal of Physical Organic Chemistry Volume 20, Issue 8, pages 589-593, August 2007.

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