

T-shaped unsymmetrical azoester based mesogenic dimers

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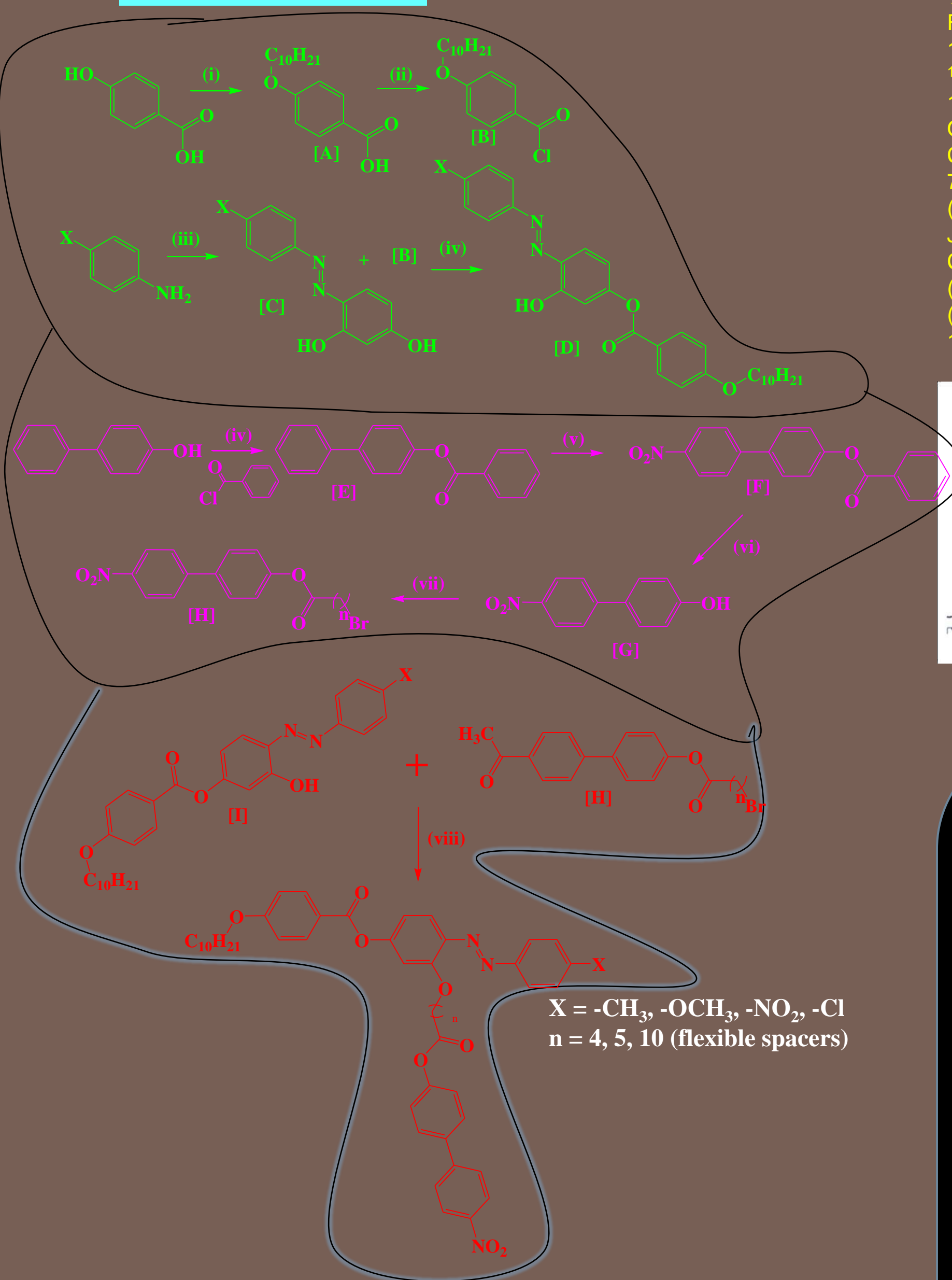
Introduction

There could be several potential applications of LC dimers due to their distinct nature and unusual properties. Both symmetric and non-symmetric dimers exhibit a rich smectic polymorphism. Blatch et al reported the non-symmetric dimers from cyanobiphenyl mesogen connected to a cinnamate moiety through a flexible spacer which exhibited as intercalated smectic A phase. Jin et al have studied in detail the smectic phase behaviour of non-symmetric dimers containing a cholesteryl unit linker to a conventional calamitic mesogenic unit via a flexible alkyl spacer. Several examples of non-symmetrical charge-transfer dimers in which a triphenylene-based unit is connected to an electron-deficient non-liquid crystalline THF of anthraquinone moiety. The synthesis of dimer, in which there is an amide group in the linking chain, was reported by Boden et al. An interesting example of non-symmetric discotic donor- σ -acceptor dimer reported by Kumar et al. The strong nematic tendencies of the T-shaped dimers implies that the spacer adopts conformations for which the two mesogenic units are held more or less coparallel. This view is supported by the weaker dependence of the spacers seen for the T-shaped dimers that observed for conventional linear dimers. Nori et al have reported the purely nematogenic T-shaped compounds which having the polymethylene spacers with six benzene bridging through the four ester group. Yoshizawa et al have designed novel T-shaped and bent chiral compounds possessing molecular biaxiality, and investigated the chirality-dependent properties. Weissflog et al have reported the T-shaped compounds with having the nematic mesophases and smectic A mesophases.

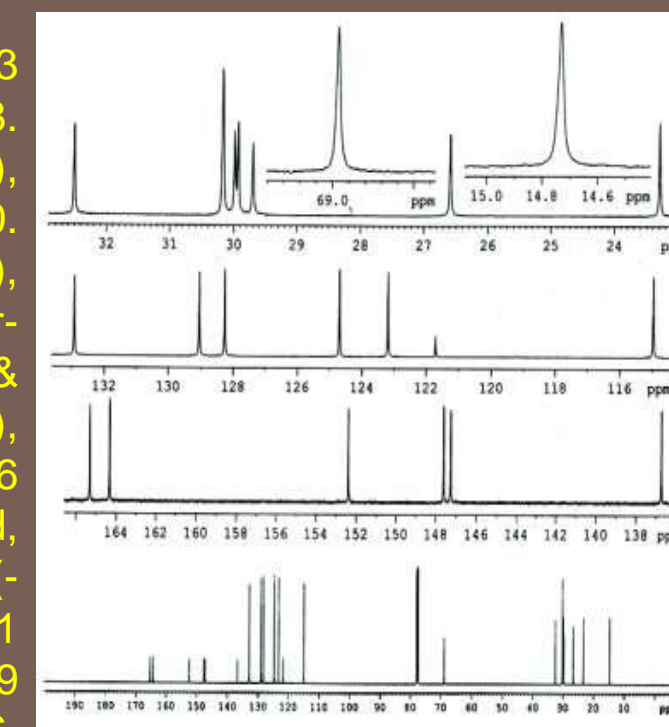
Aims and objective

Azobenzene molecules are of special interest as photoisomerization reaction can bring in-situ changes in the molecular architecture resulting in interesting behaviour. Additionally, the molecules with azobenzene group find application in photomechanical devices. Liquid crystals containing azobenzene group are promising materials for devices involving photomechanics, optical switching and image storing because of their high resolution and sensitivity. Biphenyl derivatives exhibit rich mesomorphism. Azoester-central linkage imparts very high thermal stabilities. One mesogenic series of T-shaped unsymmetrical dimers with biphenyl nucleus have been synthesized which differ by the number of methylene units in the flexible spacers and terminal substituent in the main core.

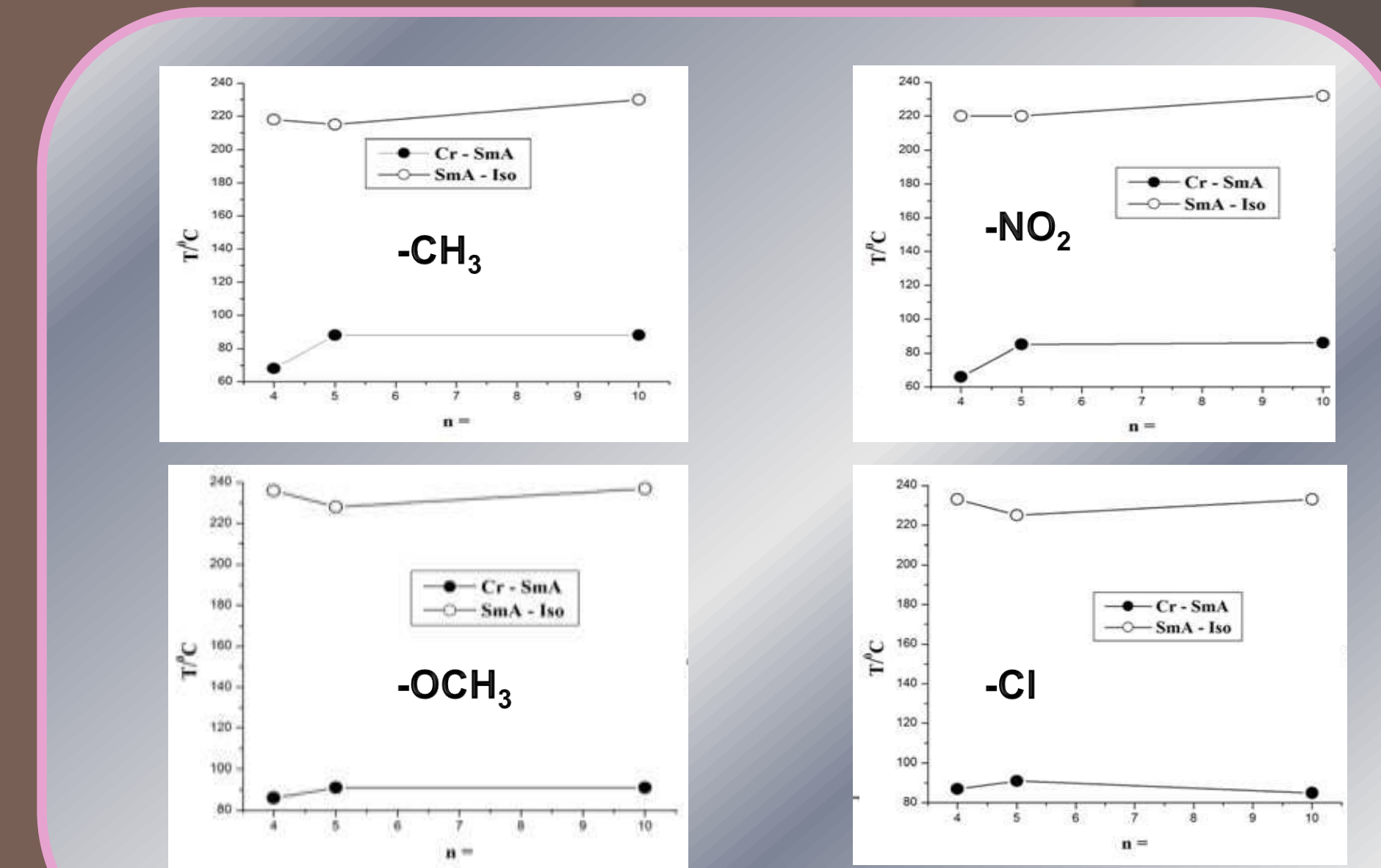
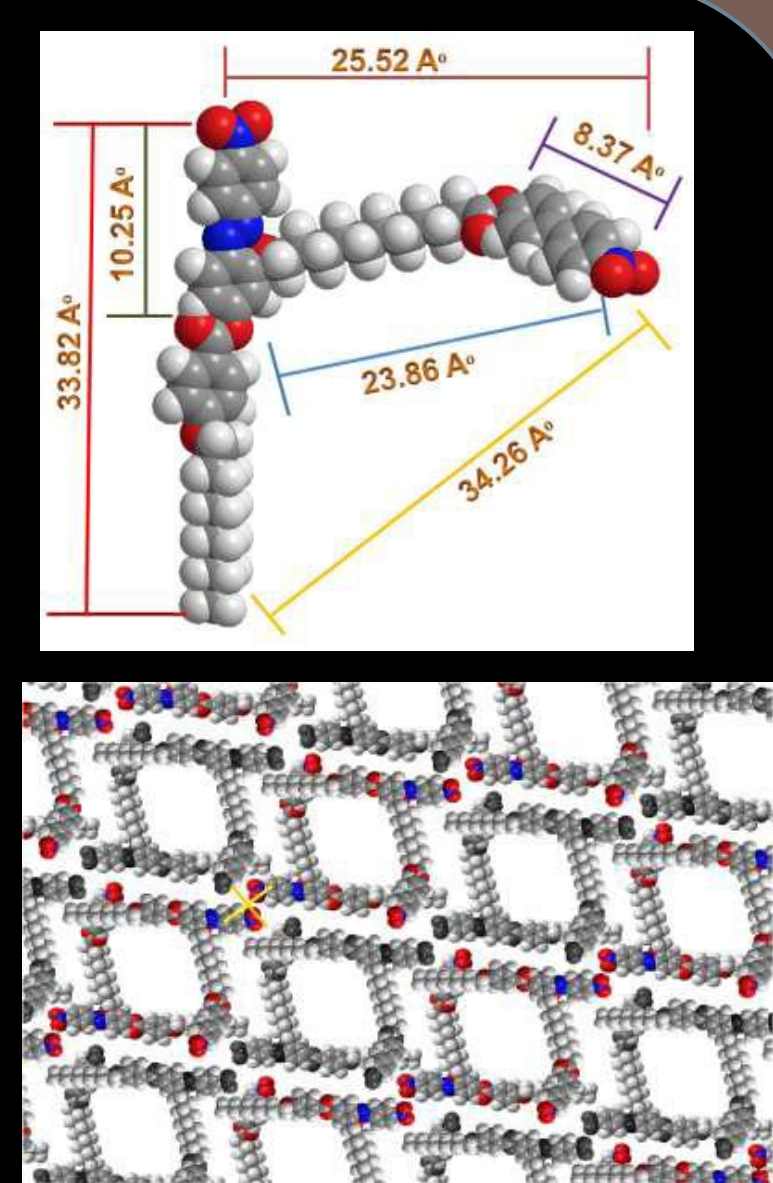
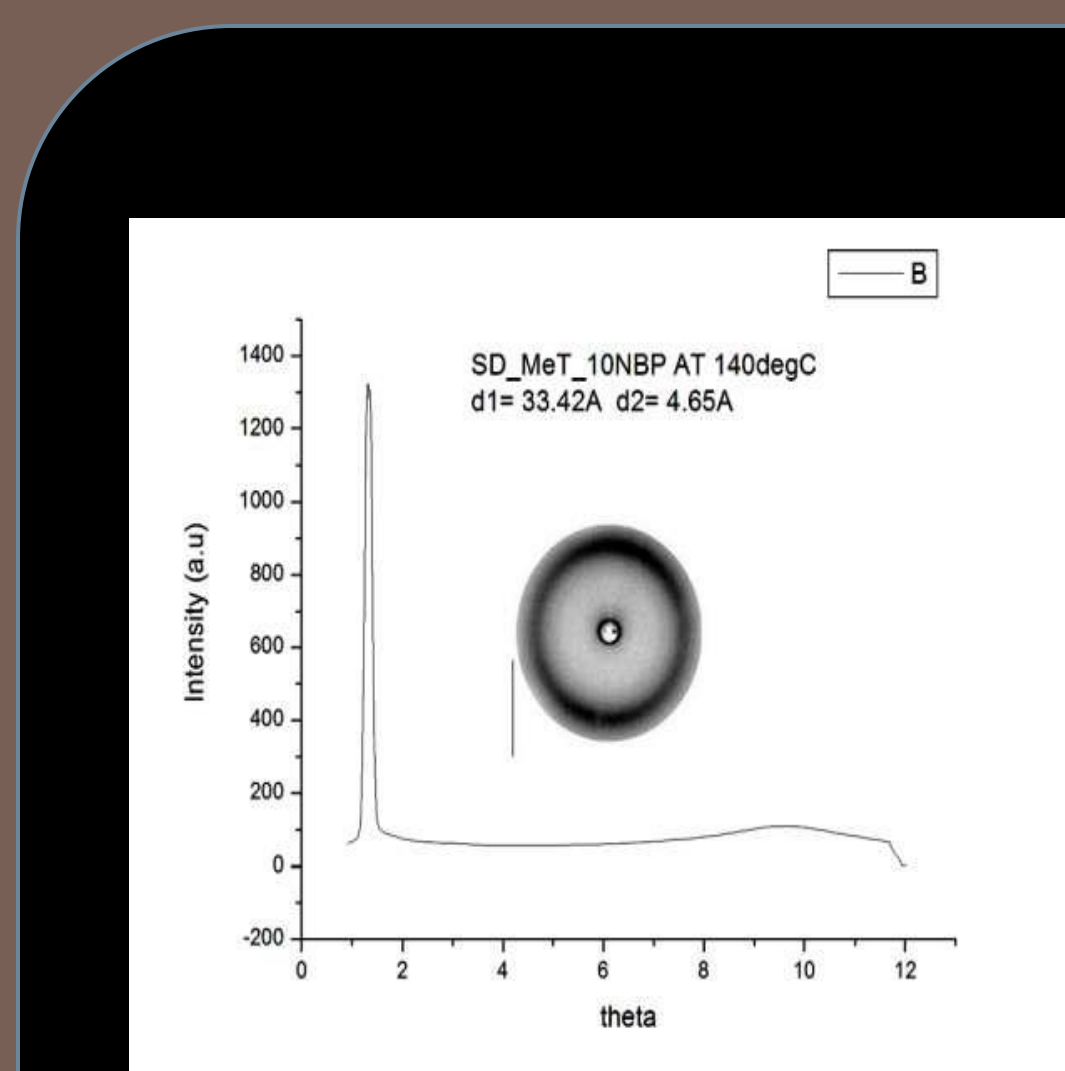
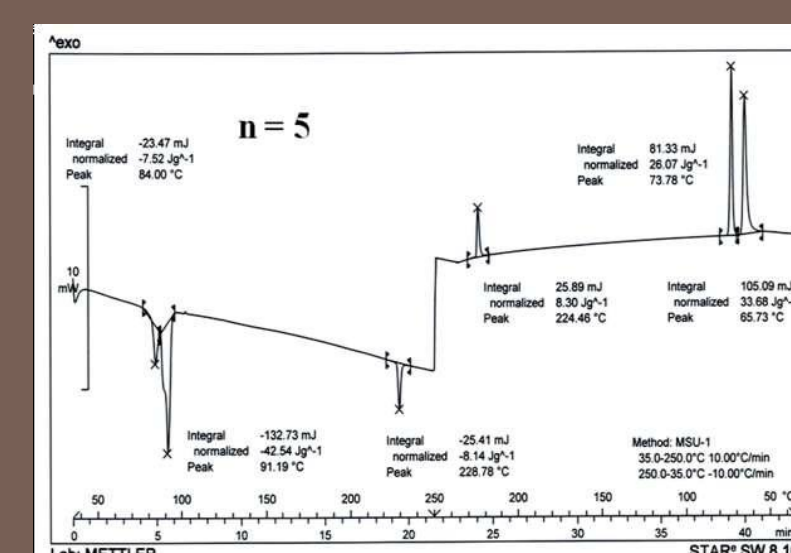
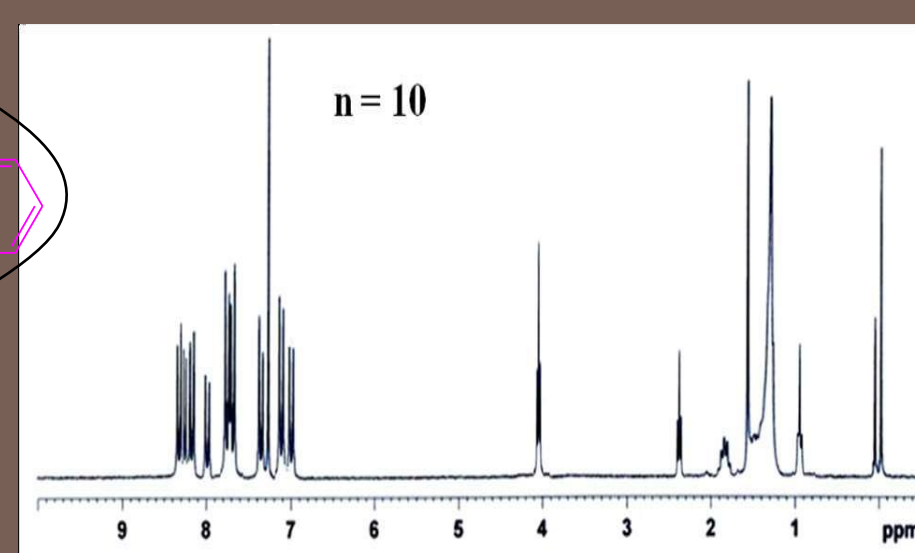
Experiment:



(X = -NO₂, n = 10): Elemental analysis: C₄₆H₄₈N₄O₁₀; found 67.55 %C, 5.85 %H, 6.83 %N for 67.57 %C, 5.87 %H, 6.85 %N; UV spectrum (MDC) nm: 266, 369 and 438. FTIR (KBr) ν /cm⁻¹: 2959, 2918, 2860 (-CH₂-COO-Ar), 1715 (Ar-COO-Ar), 1601 (-N=N-), 1550, 1510, 1435, 1400, 1320, 1280 (Ar-O-C-), 1210, 1170, 1110, 1050, 1007, 830, 800. ¹H NMR (400MHz): δ 0.89 (t, 3H, -CH₃), 1.28-1.49 (m, 16H, Ar-O-C-C-(CH₂)₁₃- at C-4''), 1.56-1.89 (m, 6H, Ar-OCO-C-CH₂- & Ar-O-C-CH₂- at C-1 & C-4''), 2.26 (t, 2H, Ar-OCOCH₂-), 4.07 (t, 2H, Ar-O-CH₂- at C-4''), 6.97 (d, J=9.0Hz, 4H, ArH at C-4, C-6, C-3' & C-5''), 7.19 (d, J=8.5Hz, 2H, ArH at C-a & C-b), 7.33 (d, J=8.9Hz, 2H, ArH at C-b & C-c), 7.64-7.77 (m, 3H, ArH at C-3, C-e & C-h), 8.04 (d, J=8.8Hz, 2H, ArH at C-2' & C-6''), 8.16 (d, J=8.7Hz, 2H, ArH at C-2' & C-6''), 8.23 (d, J=8.8Hz, 2H, ArH at C-f & C-g), 8.30 (d, J=8.9Hz, 2H, ArH at C-3' & C-5''). ¹³C NMR (500MHz, CDCl₃): δ (-CH₃(q), 14.72 (C), (-CH₂- (t), 23.28 (2C), 26.58 (2C), 29.55(2C), 29.69 (2C), 29.92 (3C), 29.97 (2C), 30.31 (4C), 32.49 (2C)), (-CH- (d), 115.17 (4C), 117.28, 118.10, 119.20, 123.19 (4C), 124.69 (4C), 1332.91 (4C)), (-C- (q), 121.60, 129.25 (3C), 130.83 (3C), 136.73, 147.61, 147.26, 152.39, 164.32, 165.31).



Sr. No.	Substituent :	n =	Transition temperatures (t ^o C) and enthalpy values [ΔH /kJ mol ⁻¹]	
			Heating	Cooling
1	X = -CH ₃	4	Cr 68 SmA 218 Iso	Iso 217 SmA 65 Cr
2	X = -CH ₃	5	Cr ₁ 83.18 [2.94] Cr 88.29 [30.79] SmA 215.26 [9.61] Iso	Iso 212.16 [13.24] SmA 56.93 [79.66] Cr
3	X = -CH ₃	10	Cr 88 SmA 230 Iso	Iso 227 SmA 84 Cr
4	X = -OCH ₃	4	Cr 79.86 [99.92] SmA 235.41 [13.92] Iso	Iso 231.11 [15.08] SmA 52.10 [21.42] Cr 46.38 [1.88] Cr ₁
5	X = -OCH ₃	5	Cr ₁ 83.94 [10.01] Cr 91.51 [47.83] SmA 229.99 [13.67] Iso	Iso 225.53 [13.08] SmA 67.02 [18.06] Cr 62.49 [31.24] Cr ₁
6	X = -OCH ₃	10	Cr 88 SmA 230 Iso	Iso 227 SmA 84 Cr
7	X = -NO ₂	4	Cr 86 SmA 236 Iso	Iso 235 SmA 89 Cr
8	X = -NO ₂	5	Cr ₁ 84.00 [9.91] Cr 91.19 [56.06] SmA 228.78 [10.72] Iso	Iso 224.46 [10.94] SmA 73.78 [34.36] Cr 65.73 [44.38] Cr ₁
9	X = -NO ₂	10	Cr 91 SmA 237 Iso	Iso 235 SmA 89 Cr
10	X = -Cl	4	Cr 87 SmA 233 Iso	Iso 232 SmA 85 Cr
11	X = -Cl	5	Cr ₁ 83.17 [24.32] Cr 91.04 [71.03] SmA 229.47 [13.20] Iso	Iso 225.57 [15.32] SmA 70.68 [31.77] Cr 65.79 [87.92] Cr ₁
12	X = -Cl	10	Cr 85 SmA 223 Iso	Iso 230 SmA 84 Cr



Phse behaviour

Conclusions

✓ Although many laterally linked, 'T-shaped', twin LC compounds with various flexible spacer (n = 4, 5, 11) and substituted biphenyl nucleus have been investigated in this study, their ability to form mesophases appears to be less than for the corresponding linearly joined dimesogenic compounds with the same or similar mesogens.

✓ All of the experimental results and discussion lead us to the conclusion that the present system of T-shaped dimesogenic compounds forms SmA mesophase.

✓ All the T-shaped dimers with methoxy group exhibit higher thermal stabilities than do methyl group. The nitro terminal substituents exhibited higher thermal stability as compared to chloro terminal substituents.