Liquid Crystals

Bent-shaped liquid crystals containing a furan bridge in the mesogenic core

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# Bent-shaped liquid crystals containing a furan bridge in the mesogenic core

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We report the synthesis and characterization of hitherto unreported bent-shaped dimeric liquid crystals based on a furan bridge in the mesogenic core. The compound **18-Fu2** exhibits liquid crystalline behaviour.
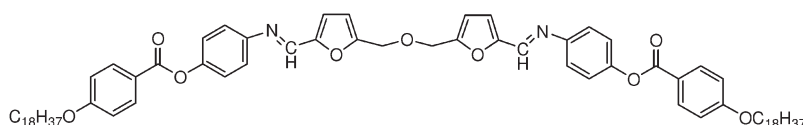
1. Introduction

Materials consisting of bent-shaped molecules, which exhibit the so-called banana mesophases, chirality and respond to an electric field to exhibit ferroelectric/antiferroelectric properties, are of current scientific interest and technological applications [1, 2], such molecules comprise a new subfield of thermotropic liquid crystals [3, 4]. These bent-shaped molecules are derived from two molecular fragments (either mesogenic or non-mesogenic) connected to a central core consisting of either an aromatic ring [3, 4] or an aliphatic alkylene moiety [5–7], either through an ester or imine linkage in the majority of cases. Such compounds, when linked through a flexible aliphatic spacer, are recognized as dimeric liquid crystals and exhibit unusual mesophase behaviour, which is distinctly different from that of corresponding molecular fragments [8, 9]. Watanabe *et al.* [10, 11] reported interesting mesophases exhibited by the dimeric systems depending upon the number of carbon atoms (parity) in the spacer joining the two aromatic fragments possessing terminal chains. Furthermore such achiral systems exhibit antiferroelectric or non-ferroelectric switching behaviour under the influence of a triangular wave electric field, provided the odd alkylene spacer (promoting

bent shape) and terminal chains of the dimer segregate to form smectic layers. These dimeric molecules also exhibit macroscopic polar order under the influence of an electric field which is confirmed by second harmonic generation studies [12].

Symmetric dimeric molecules can be regarded as model compounds for polymeric liquid crystals [5]; also referred to as twin dimers, they consist of three different units, namely alkyl(oxy) end chains, the conjugated mesogenic core and an alkylene spacer. The conformational constraint due to the alkylene spacer and the random mixing of the spacers and terminal alkyl chains are the two important factors deciding the molecular structural arrangement and the nature of smectic phases. Depending on the terminal chain length (carbon number=n) of the dimeric molecule linked through an odd-numbered alkyl chain spacer (pentyl), the compounds exhibit monolayer ($n<7$), frustrated ($n=8$) or bilayer ($n>10$) smectic liquid crystalline behaviour [8]. Furthermore the steric incompatibility of the central alkylene spacer with the terminal alkyl chains promotes the bilayer molecular structure with two mesogenic layers in a repeat unit. The presence of the mesogenic layers in a repeat unit leads either to synclinic or anticlinic molecular arrangement depending on the parity of the spacer.

In a dimeric system the confined orientational correlation of the mesogenic or non-mesogenic moieties exists only within the dimer molecule. When the alkyl

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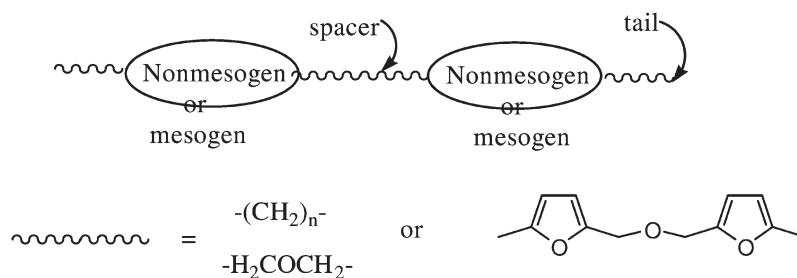*Corresponding author. Email: nvsrao@sancharnet.in

Figure 1.   Model of dimer molecule and possible bridging groups.

chain length is varied the compounds exhibit subtle and complex phase behaviour. The dimeric compounds are essentially different from the polymers with respect to the molecular length or number density of the molecular ends. However when the central linking group is separated by a hetero atom, the structure–property relationships are much more complicated and new phases may result. As a part of continuous effort to realize new materials to explore the limits of molecular shapes compatible with liquid crystalline behaviour, and to study structure–property relationships, we report here the synthesis and characterization of the dimeric mesogen based on a furan bridge in the core, see figure 1.

2.   Experimental

Several furan-based derivatives were synthesized using standard synthetic procedures as illustrated in scheme 1. Sucrose was converted into furan-based

dialdehyde [13], which was then heated under reflux with 4′-aminophenyl 4-alkyloxybenzoate in absolute ethanol in the presence of a catalytic amount of glacial acetic acid to afford the desired product *n*-**Fu2**. The molecular structures of all the compounds were confirmed by elemental analysis, mass spectroscopy, proton nuclear magnetic resonance and infrared spectroscopy; structural characterization data of 18-Fu2 are presented as a representative example. UV λ_{max}: 276, 330 nm. IR ν_{max}: 1255, 1630($\nu_{C=N}$), 1733($\nu_{C=O}$), 2850, 2916(ν_{CH}) cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz) : δ 8.32 (s, 2H), 8.09 (d, $J=8.4$ Hz, 4H), 7.27 (d, $J=6.5$ Hz, 4H), 7.20 (d, $J=9.0$ Hz, 4H), 7.00–6.97 (m, 6H), 6.58 (d, $J=3$ Hz, 2H), 4.65 (s, 4H), 4.04 (t, $J=6.6$ Hz, 4H), 1.84–0.86 (m, 70H, aliphatic **H**). MS m/z 1162 (M$^+$). Anal: calcd for C$_{74}$H$_{100}$O$_9$N$_2$. C 76.51, H 8.68, N 2.41; found, C 76.2, H 8.87, N 2.37%. CHN analysis was carried out on PE-2400 series-II CHN analyser.
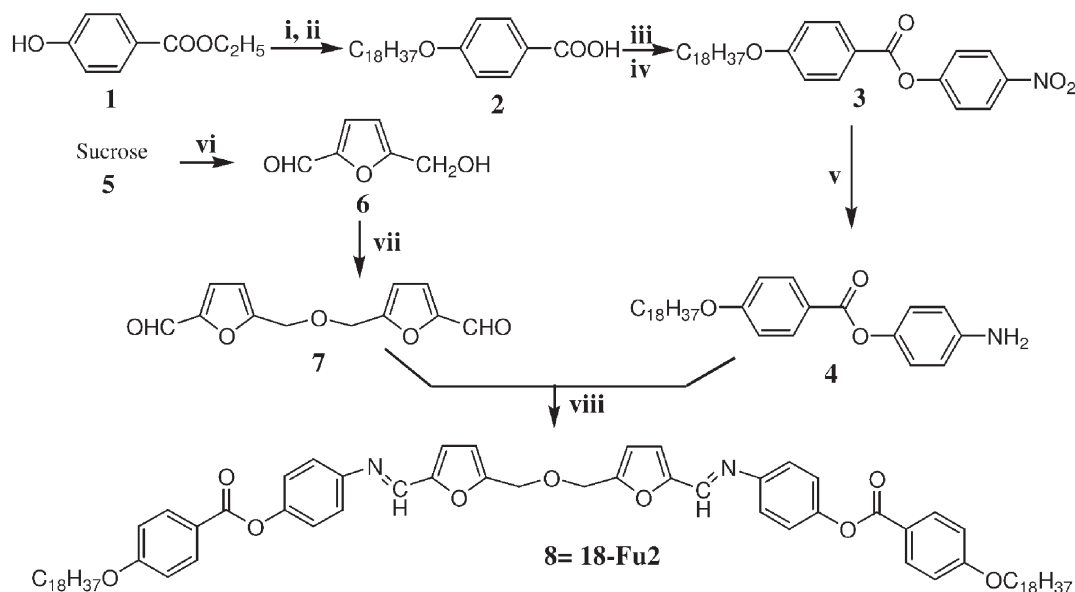
Scheme 1.   Reaction conditions and reagents: (i) absolute alcohol, KOH, C$_{18}$H$_{37}$Br, KI, Δ, 36h; (ii) OH$^-$/H$_2$O; (iii) SOCl$_2$, reflux, 1h; (iv) 4-nitrophenol, DCM, aq K$_2$CO$_3$, Bu$_4$NHSO$_4$, 12h; (v) 10%Pd/C(cat) EtOH, rt, 12h; (vi) oxalic acid, H$_2$O, 145°C, 50 psi; (vii) tolune sulphonic acid, Δ, tolune, 1h; (viii) absolute EtOH, glacial AcOH, Δ, 3h.

Table 1. Phase transition temperatures (°C), and associated enthalpies (ΔH, kJ mol^{-1}) and entropies (Δs, kJ mol^{-1} K^{-1}) of **18-Fu2**.

Phase Transition	1st heating/cooling, 10°C min^{-1}			2nd heating/cooling, 5°C min^{-1}			3rd heating/cooling, 10°C min^{-1}		
	T	ΔH	ΔS	T	ΔH	ΔS	T	ΔH	ΔS
Cr^1–Cr^2				68.7	1.22	3.57	68.7	0.26	0.77
Cr^2–Cr^3	74.7	0.31	0.89	73.8	0.62	1.81	74.1	1.73	5.02
Cr^3–Cr^4				79.8	0.89	2.52	80.3	1.01	2.86
							109.6[a]	1.17	3.07
Cr^4–Cr^5	113.9	2.43	6.27	114.8	0.70	1.80	115.7	0.51	1.32
Cr^5–SmX	125.3	47.35	118.8	120.9	8.37	21.27	121.8	9.32	23.6
SmX–I	155.4	71.09	165.9	151.7[b]	47.41	111.6	151.4[b]	39.14	92.2
I–SmX1	144.3	51.92	124.3	143.8	14.52	34.8	142.9	11.58	27.8
SmX1–SmX2				141.1	12.43	30.0	139.9	9.02	21.8
SmX2–Cr^3	119.1	7.43	18.9	119.0	6.37	16.2	118.6	5.96	15.2
Cr^3–Cr^2	114.4	0.53	1.36	114.5	0.87	2.25	114.3	0.98	2.55
				106.8[a]	1.03	2.72			
Cr^2–Cr^1	76.1	1.00	2.86	76.3	0.91	2.63	75.7	1.25	3.59

[a]Crystal–crystal transition observed in heating/cooling cycle and not repeated in cooling/heating cycle. [b]Two smectic–smectic transitions are smeared and detected as a single smectic–isotropic transition

3. Results and discussion

The **n-Fu2**-based mesogens reported here differ from the dimeric materials reported by others [3–10]. The furan rings are free to move and the flexible ether spacer makes them non-rigid. However there are three non-compatible units in the molecule, which promote interactions between different molecular functional segments, viz. terminal alkyloxy chains, aromatic cores linked to a furan ring, and the central ether linkage.

The transition temperatures and associated enthalpies of compound **18-Fu2** determined by differential scanning calorimetry (DSC) are presented in table 1. In the DSC scan (figure 2) we observed several solid–solid
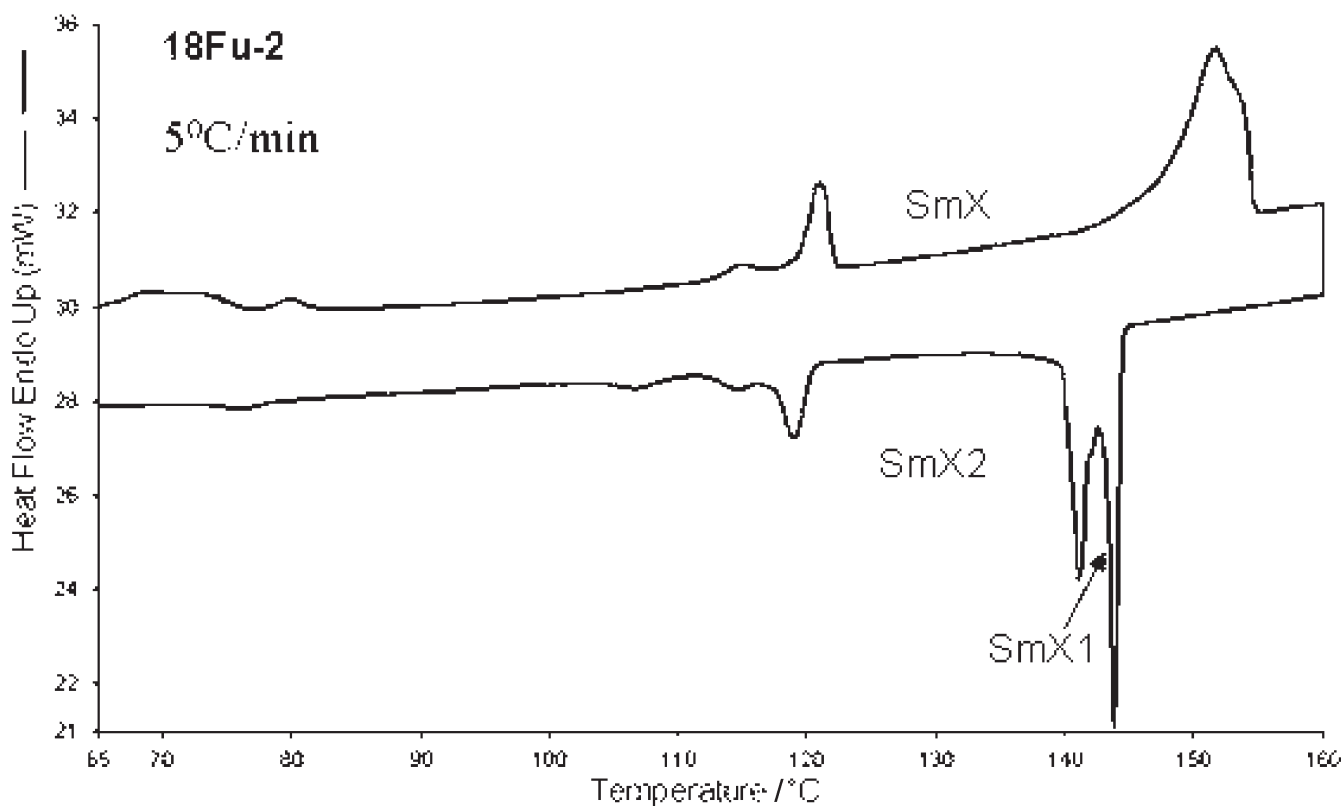

Figure 2. DSC thermogram of **18-Fu2** obtained in the second heating/cooling cycles at 5°C min^{-1}.

(and/or crystalline smectic–smectic) transitions below 120°C with small but noticeable enthalpy changes ($<2\,kJ\,mol^{-1}$), which were not observed by thermal microscopy. The solid–liquid crystal phase transition recorded in the heating cycle by DSC is confirmed by thermal microscopy. However the liquid crystal–isotropic transition is not well resolved in the heating cycle (possibly two transitions are smeared because of the small thermal range and relatively high scanning rates), and the enthalpy recorded at the smectic–isotropic transition is much higher than for the solid–smectic phase transition, which is common in bent-shaped liquid crystalline materials. The difference in enthalpy values from first and subsequent heating/cooling cycles is probably due to the ordered arrangement of molecules within each layer which must have

been driven by minimized steric packing forces as well as minimization of Coulombic free energy to an ordered arrangement of the molecules that sets-in during the solidification process.

A sample **18-Fu2** on heating exhibited no known characteristic textures. On very sow cooling a variety of texture variants was seen but mostly they appeared simultaneously within the same preparation and were paramorphotic with decreasing temperature. These textures are presented in figures 3 (*a–d*). On slow cooling from the isotropic phase the sample exhibited a non-specific grainy fan-like, thin striped texture with arcs, as shown in figure 3 (*a*) (145.1°C), but with more homeotropic regions just below the isotropic–mesomorphic transition. The texture with arcs grows from filament like lines arranged in a circular pattern in

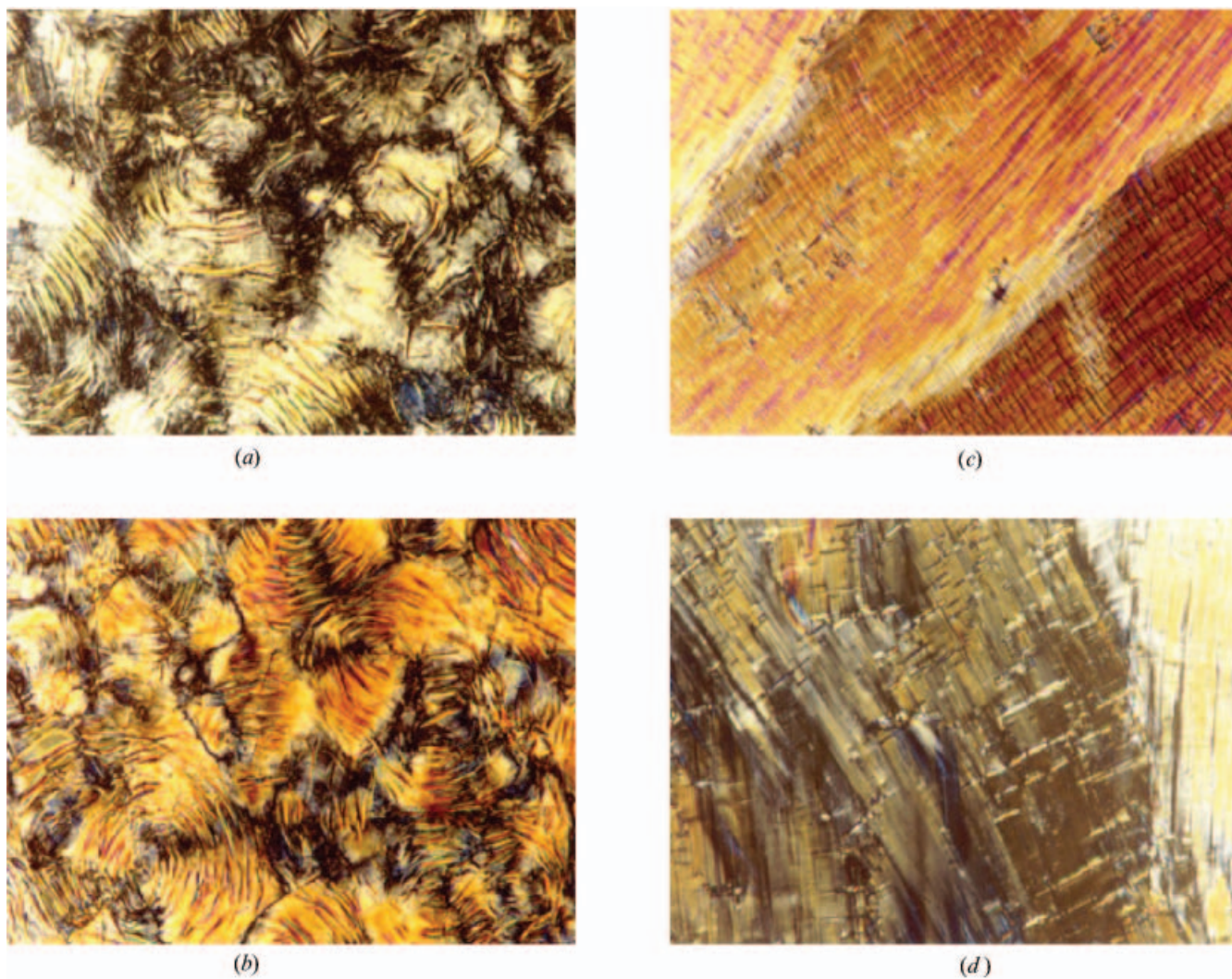Figure 3.	(*a*) Striated arc-like texture at 145.1°C; (*b*) striated arc-like texture at 145.1°C after shearing; (*c*) fan-like texture at 140.0°C with lines across the fans; (*d*) fan-like texture with mosaic boundaries with lines across the fans.

stripes radiating from a point with alternate domains. These domains are formed as stripes along the smectic layers. The optical extinction of the neighbouring stripes appears to be symmetrical along the smectic layers. The sample on shearing exhibited a similar type of texture but with different colours, figure 3 (*b*). The appearance of the phase does not resemble any known texture [16] but it may be premature to attribute any of the different B2 type phases reported in literature. This form of alternating domains is an indication of synclinic or anticlinic molecular arrangement. This may be due to the molecular arrangement of the central bent core and aliphatic alkyl end chains which are incommensurate with each other. On further cooling the sample exhibited a fan-like texture with fine lines across the fans as shown in figure 3 (*c*) (140.0°C). Further cooling of the sample leads to the mosaic-like texture shown in figure 3 (*d*) (125.0°C). Moreover in higher homologues the texture is prominently dominated by homeotropic regions, which may be because of the possible orientation of homeotropic alignment of long alkyl chain compounds.

It is conceivable that the domain like transition bars, which are not transient, across the observed texture in this compound, resemble the texture observed in the crystal E phase [7] of a dimeric molecule or a metallomesogen [15]. However there is absolutely no reason to believe that the observed texture is identical to the reported texture of crystal E phase. Furthermore the sample is highly viscous and may be any of the highly ordered banana smectic or crystalline phases. The occurrence of the fan-shaped texture suggests a layered (smectic) structure. Moreover the fan texture in higher homologues when $n > 10$ exhibits stripes rather than clear focal fans as observed in lower homologues.

In general, the achiral banana-shaped molecular systems that generate reduced symmetry mesophases normally consist of at least five or more aromatic rings. In our present study the compound **18-Fu2** possesses a six-ring structure separated by an ether linkage which can assemble as bent or banana-shaped because of a restricted non-planar propeller-like conformation and hence would be expected to generate banana phases rather than conventional mesomorphism. We continue work to obtain a clear picture of the liquid crystalline behaviour of this new class of organic mesogens and a full account will be communicated later.

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