Utilising Saturated Hydrocarbon Isosteres of *para* Benzene in the Design of Twist-Bend Nematic Liquid Crystals

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Abstract

The nematic twist-bend (N_{TB}) liquid crystal phase possesses a local helical structure with a pitch length of a few nanometres and is the first example of spontaneous symmetry breaking in a fluid system. All known examples of the N_{TB} phase occur in materials whose constituent mesogenic units are aromatic hydrocarbons. It is not clear if this is due to synthetic convenience or a *bona fide* structural requirement for a material to exhibit this phase of matter. In this work we demonstrate that materials consisting largely of saturated hydrocarbons can also give rise to this mesophase.

Furthermore, we find that replacement of 1,4-disubstituted benzene with *trans* 1,4-cyclohexane or 1,4-cubane does not especially alter the transition temperatures of the resulting material nor does it appear to impact upon the heliconical tilt angle. Each of these three units is effectively rigid and linear; calculating the probability distribution of bend angles for each compound reveals that the isosteric groups has little impact on the overall molecular shape, demonstrating the shape-driven nature of the N_{TB} phase. Conversely, we find that incorporation of 2,6-disubstituted cuneane – a saturated hydrocarbon which is rigid but not linear – supresses the formation of the N_{TB} phase.

Introduction

Liquid crystals are a collection of states of matter (mesophases) which possess orientational and/or positional order not found in the liquid state. Different LC mesophase are principally characterised by their degree of positional order; the nematic LC phase possesses long range orientational order, whereas smectic phases also exhibit positional order in one dimension. The discovery of nematic phases in which the average orientational order varies periodically – so called modulated nematics – has recently attracted significant interest. [1-6] The twist-bend nematic phase (N_{TB}) exhibits a heliconical precession of the nematic director through space with a periodic length scale of a few

tens of nanometers. [7-9] This phase is typically found in materials comprising two or more mesogenic units which are mutually appended by a central spacer of such a length as to impart a gross bent shape. The incidence of the N_{TB} phase is intimately linked to molecular shape, specifically the bend angle between adjacent mesogenic units. [10-14] The mesogenic units themselves are almost exclusively constructed from multiple benzene rings, and to date (as far as the authors are aware) the spacer is always appended to an aromatic ring rather than a saturated hydrocarbon; [15-23] it is not clear if this is a consequence of synthetic convenience or a real structural requirement for materials to exhibit this phase of matter.

There is evidence to suggest that the occurrence of N_{TB} phases is a consequence of molecular shape; [12, 13] assuming this to be true, we considered that it should be possible to incorporate isosteric replacements for *para* substituted benzene rings without detriment to the incidence of these modulated nematic phases. There are a number of saturated hydrocarbons can be considered as isosteric with *para* substituted benzene, [24, 25] and while 1,4-disubstituted *trans* cyclohexane and bicyclo[2.2.2]octane [26, 27] are known within the context of liquid crystalline matter, others - such as 1,4-disubstituted cubane – remain largely obscure in this field. [28, 29] 1,4-Cubanes can undergo metal-catalyzed σ-bond rearrangement in the presence of silver salts to afford 2,6- and 1,3- disubstituted cuneanes (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octanes), [30, 31] with a small number of liquid crystalline derivatives of this wedge-shaped saturated hydrocarbon being known. [32] The replacement of benzene with such saturated isosteres is generally detrimental to the liquid crystalline state, [33, 34] however we considered that the shape-driven nature of the N_{TB} phase means it should be possible to replace *para*-substituted benzene rings with linear non-conjugated hydrocarbon isosteres without detriment to the incidence of this phase. Conversely, non-linear motifs such as 2,6-disubstituted cuneane would be expected to inhibit the formation of the N_{TB} phase.

Experimental

In this work we used commercially available *trans trans* 4'-(but-3-enyl)-4-(3,4-difluorophenyl)bicyclohexane (**1**, TCI UK) as a mesogenic unit; a five step synthesis gave the trimers **J4$_{hex}$, J4$_{phen}$,** and **J4$_{cub}$,** which contain either a 1,4-substituted *trans* cyclohexane, 1,4-substituted benzene, or 1,4-substituted cubane unit in the centre of the middle mesogenic unit. Hydroboration of **1** with 9-BBN and oxidation of the intermediate alkylborane afforded the alcohol terminated material (**2**) in good yield, as described by Hiyama *et al*. [35] Etherification of 2 with 4-tertbutyldimethylsilyloxyphenol, prepared according to Li *et al*, [36] followed by desilylation with TBAF afforded the phenolic intermediate (**3**) in acceptable yield. Subsequent esterification of **3** with either *trans* 1,4-cyclohexanedicarboxylic acid (SigmaAldrich), terephthalic acid (Fluorochem), or

cubane-1,4-dicarboxylic acid [28, 37] afforded **J4hex, J4phen,** and **J4cub**, respectively, as shown in scheme 1. Quantitative conversion of **J4cub** to the 2,6-dicuneane analogue (**J4cun**) was achieved by the action of silver triflate in refluxing anhydrous toluene with exclusion of light, [30, 31] followed by standard purification techniques. The degree of conversion is quantifiable by ^{1}H NMR *via* integration of the cubane C$\underline{H}$ resonance (4.43 ppm) versus the C$\underline{H}$ resonances of 2,6-cuneane (3.25 - 3.40 ppm); we observe quantitative conversion within five hours.
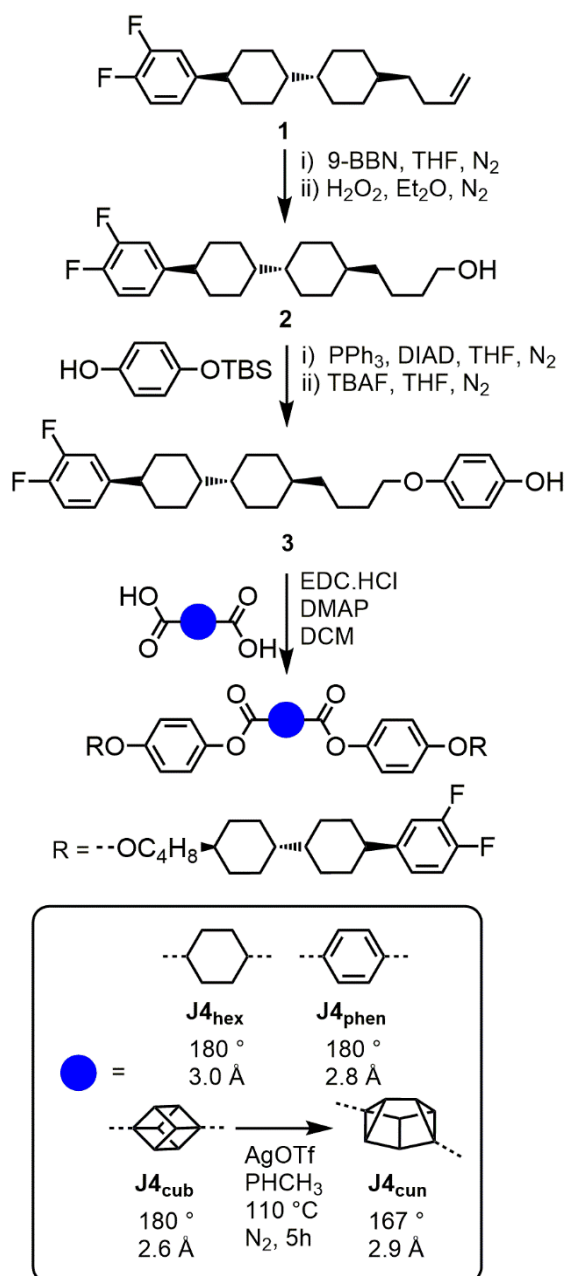
Scheme 1

Results

The transition temperatures of all four materials were determined by a combination of polarised optical microscopy (POM) and differential scanning calorimetry (DSC), and are presented in Table 1.
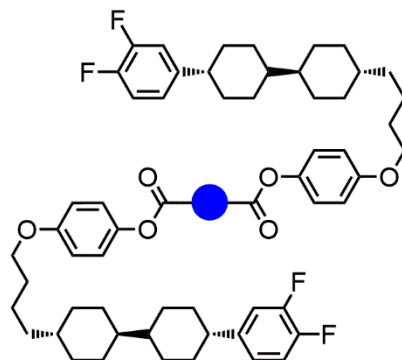
| No.	● =		MP	N_{TB}-N	N-Iso
J4$_{hex}$	(cyclohexane)	T	169.3	159.8	285.5
		ΔH	35.1	0.1	2.9
J4$_{phen}$	(benzene)	T	178.8	166.2	304.6
		ΔH	60.5	0.1	3.5
J4$_{cub}$	(cubane)	T	174.4	163.9	>230*
		ΔH	32.5	0.1	-
J4$_{cun}$	(cuneane)	T	162.2	-	>230#
		ΔH	67.5	-	-

Table 1: Transition temperatures (T, °C), and associated enthalpies of transition (ΔH, kJ mol^{-1}) as determined by DSC at a heat/cool rate of 10 °C min^{-1}. * Both **J4$_{cub}$** and **J4$_{cun}$** undergo decomposition when heated beyond 230 °C.

All materials exhibit nematic and twist-bend nematic (N_{TB}) mesophases, with the exception of **J4$_{cun}$** which displays a nematic phase only. Phase assignment was made based on the optical textures observed during POM (Figure 1). The magnitude of the enthalpy associated with the N_{TB}-N and N-Iso transitions is consistent with our phase assignment. The phase assignment of N_{TB} is also supported by X-ray scattering experiments (see later and ESI). It is notable that not only do these three materials exhibit nematic and N_{TB} phases but that the transition temperatures are also largely invariant, irrespective of the isostere employed. We find **J4$_{hex}$** and **J4$_{phen}$** have comparable clearing points whereas the cubane derivative **J4$_{cub}$** decomposes on heating above ~ 230 °C and so we could

not determine a clearing point; however, that cubane undergoes pyrolysis at these temperatures is known. [38, 39] The 2,6- disubstituted cuneane derivative **J4**$_{cun}$ is isomeric with the parent 1,4- disubstituted cubane system but is not isosteric as it lack the linearity of the analogous cubane, instead having a somewhat bent shape. As a consequence of the bend imposed on the central mesogenic unit by the 2,6-cuneane motif, material **J4**$_{cun}$ exhibits only a nematic phase. Additionally, **J4**$_{cun}$ decomposes when heated beyond 230 °C and so its clearing point could not be determined. Representative photomicrographs are presented in Figure 1.

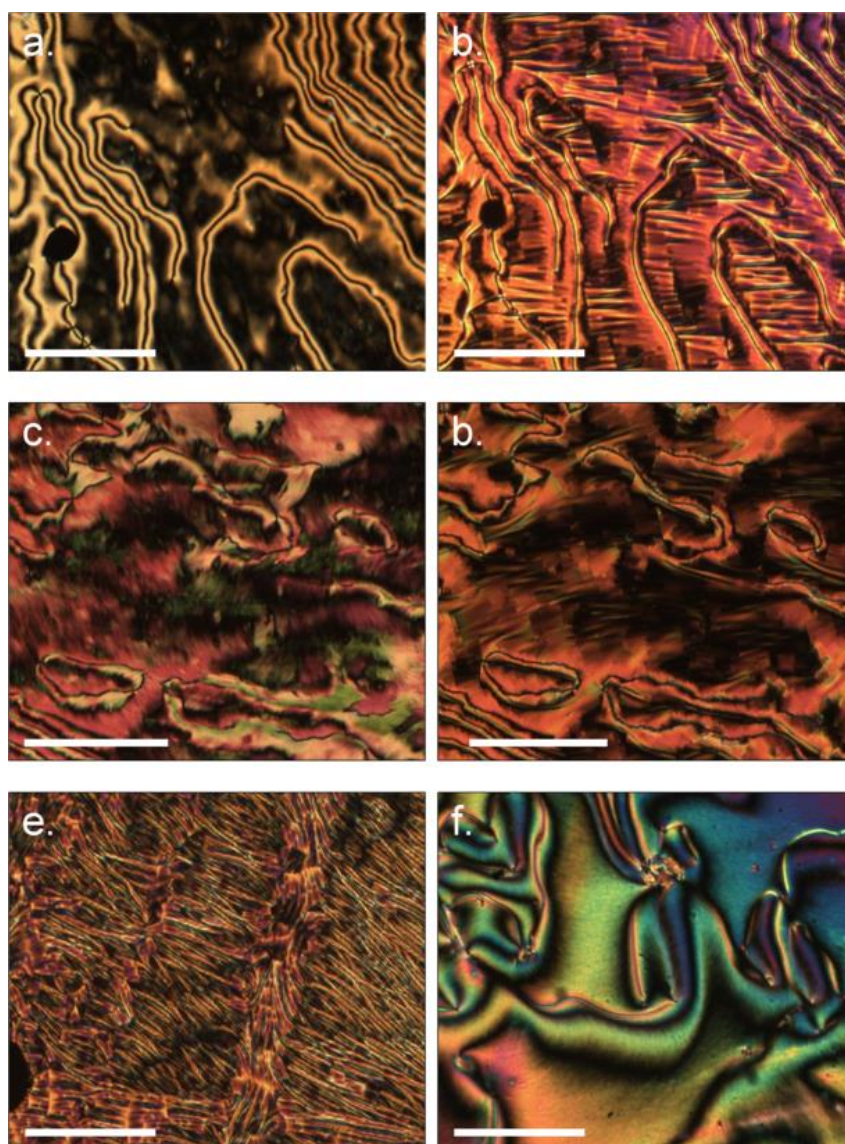**Figure 1:** Photomicrographs of: (a) the schlieren texture of the nematic phase of **J4**$_{hex}$ at 165 °C; (b) the evolving blocky/rope texture of the nematic phase of **J4**$_{hex}$ at 155 °C; (c) the schlieren/planar texture of the N phase of **J4**$_{phen}$ at 169 °C; (d) the blocky texture of the N$_{TB}$ phase of **J4**$_{phen}$ at 163 °C; (e) the rope-like texture of the N$_{TB}$ phase of **J4**$_{cub}$

at 158 °C; (f) *schlieren* texture of the supercooled nematic phase of **J4_cun** at 140 °C. Photomicrographs (a) and (b), and (c) and (d) are of approximately the same area of the sample. In all cases the scalebar corresponds to 100 μm.

We used X-ray scattering to confirm the assignment of the N_{TB} phase by measuring the heliconical tilt angle, as outlined recently; [40] as **J4_cun** exhibits a nematic phase only this material was excluded from this investigation. For all three materials that exhibit the N_{TB} phase it is monotropic and the range of supercooling short, nevertheless, we can measure the heliconical tilt angle over a short temperature range for each compound. We find that the measured heliconical tilt angles, although not saturated, do not vary significantly between the three materials in question at any given reduced temperature. This would suggest that the local structure of the N_{TB} phase is not significantly perturbed by the isosteric groups (Figure 2), which is in line with recent results. [41]
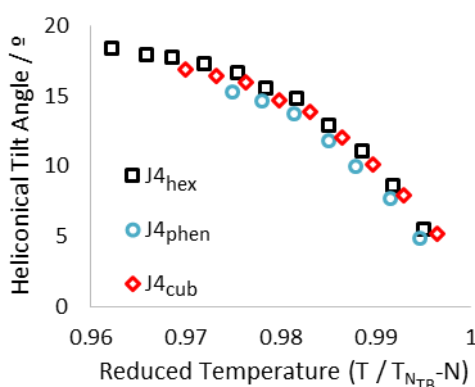
Figure 2:   The heliconical tilt angle (α, °), calculated *via* the X-ray method, as a function of reduced temperature (T_{NTB-N} / T) for **J4_hex, J4_phen** and **J4_cub**.

We next turned our attention to how these materials differ in terms of their conformational landscape. We constructed a library of conformers by allowing dihedrals in the spacer to undergo three-fold rotation as well as allowing carboxylate esters and cyclohexane-cyclohexane bonds to undergo twofold rotation, and then performing a geometry optimization within these constraints using the AM1 semi-empirical method. To reduce the number of conformers screened we studied only two thirds of the molecule (Figure 3); we find that for all four materials the possibility of 'hairpin' conformers, where the angle between the two mesogenic units is below 45 °, to be almost negligible and so this simplification is justified. For each material studied we discarded conformers whose energy was larger than that of the global minimum by 20 kJ mol^{-1} and/or had one or more

pairs of atoms closer than a cut-off distance of 0.8x the sum of their van der Waals radii. We calculated the angle between the two mesogenic units for all remaining conformers and use this to calculate a probability weighted average bend angle for each material (Figure 2). Different materials can have comparable average bend angles but different conformer distributions due a broad range of bend angles or significant populations of linear or hairpin conformers; to quantify this we fit the histogram with a Gaussian centred on the probability weighted average bend angle (Figure 3b-d, solid line). To remove the effect of histogram bin size on the FWHM we vary the number of bins from 180 to 20 and take an average. We take this average FWHM of the Gaussian fit to be a measure of the breadth of the conformer distribution (i.e. the range of populated bend angles) and so enabling comparison between materials.
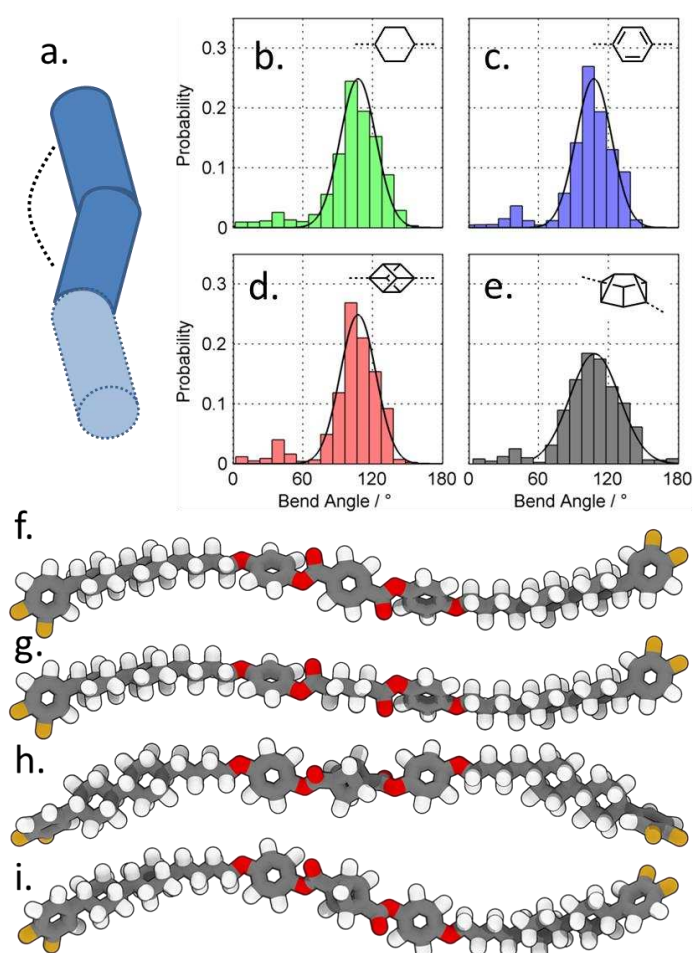
Figure 3: Calculated bend-angle probabilities obtained using the semi-empirical AM1 method for a two-thirds molecular fragment (cartoon in Fig. 3a) as described in the text for (b) **J4_hex**, (c) **J4_phen**, (d) **J4_cub**, (e) **J4_cun**, where the solid line is a Gaussian fit to the histogram; the all *trans* global energy minimum geometries for (f) **J4_hex**, (g) **J4_phen**, (h) **J4_cub**, (i) **J4_cun** optimized at the B3LYP/6-31G(d) level.

We find that the linear isosteric motifs in the central mesogenic give virtually identical average bend angles of 110 °, while the bent 2,6-disubstituted cuneane gives a slightly smaller average bend angle of 105 ° (Figure 3). The material **J4$_{hex}$** has a slightly larger FWHM (40 °) than **J4$_{phen}$** and **J4$_{cub}$** (both 30 °) and we attribute this to the non-planarity of the *trans* 1,4-cyclohexyl ring; disubstituted 1,4-benzene and 1,4-cubane are, on the other hand, planar. The three linear materials are remarkably similar in terms of their gross shape and this is reflected in the near identical transition temperatures and heliconical tilt angles. Conversely, the bent shape imparted by the 2,6-cuneane motif means a larger range of bend angles are populated by **J4$_{cun}$** and this is reflected in the FWHM of 55 °. We would suggest that any sufficiently rigid structural unit that preserves linearity could be employed in the design of materials to exhibit heliconical nematic phases. Conversely, using bent structural motifs within the mesogenic unit(s) as a way of broadening the range of bend angles populated appears to be a useful strategy for suppressing the incidence of the N$_{TB}$ phase.

As noted in the introduction, virtually all examples of the twist-bend nematic phase are found in systems containing mesogenic units constructed exclusively from aromatic rings, e.g. the CBnCB materials. Indeed, all known examples of the N$_{TB}$ phase feature a methylene spacer which is either attached directly to a phenyl ring, or *via* an intermediary linking group (e.g. ethers, imines). The novel trimers reported in table 1 illustrate that it is possible to generate this mesophase when the spacer is appended to a saturated hydrocarbon, in this case *trans* 1,4-cyclohexane. Clearly, the volume of chemical space that might be expected to give rise to the twist-bend modulated nematic phase is embiggened by this result. Present results also demonstrate that it is possible to engineer the occurrence of the N$_{TB}$ phase even when using mesogenic units that are predominantly saturated hydrocarbons. Non-trivial chemical synthesis to one side, we see no reason why the twist-bend nematic phase should not be observed in materials which are constructed *entirely* from saturated hydrocarbons.

Conclusions

We report on four novel liquid crystalline trimers, three of which exhibit nematic and twist-bend nematic mesophases and one of which exhibits only a nematic phase. These materials are the first examples of twist-bend nematogens in which the semi-flexible spacer is appended to a non-aromatic hydrocarbon. Furthermore, we demonstrate it is possible to replace *para* substituted benzene with 1,4-cyclohexane and 1,4-cubane with little change to transition temperatures or the heliconical tilt angle. Conversely, replacement with the bent 2,6-cunaene motif leads to the N$_{TB}$ phase being suppressed. We calculated the bend angles for each material as a probability weighted average of

many conformers; whereas benzene, cyclohexane and cubane containing materials have near identical average bend angles and thus mesomorphic behaviour, the conformational landscape of the 2,6-cuneane materials is notably different.

Acknowledgements

Keywords

Liquid Crystals, Nematic, Isosteres, Conformers

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