Paintbrush Terminated NTB Mesogen

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Abstract

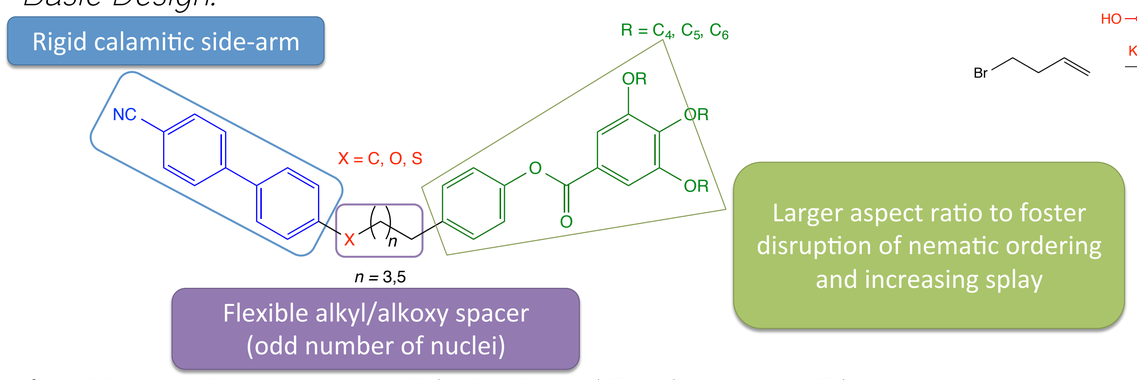
The synthesis of novel mesogens, whose architecture was based on a previously-reported nematic twist-bend (NTB) material, was affected. The *CBXCB* molecular structure of the NTB mesogen[1] was modified by replacing one of the cyanobiphenyl units with a trialkoxy gallate phenyl ester, yielding a "paintbrush terminus". The synthesis of the paintbrush terminated NTB material, and the intermediates required, were synthesized with a variety of techniques including a modified Sandmeyer coupling, and multiple Suzuki-type coupling reactions. These target molecules displayed electrooptical behaviors that deviated from that of expected NTB mesogens. It is hoped that the behavior of materials such as this will prove useful in developing theoretical calculations to predict the supramolecular structure of NTB liquid crystalline materials.

[1] Chen, D., Nakata, M., Shao, R., Tuchband, M., Shuai, M., Baumeister, U., Weissflog, W., Walba, D.M., Glaser, M.A., Maclennan, J.A., Clark, N.A. Twist-Bend Heliconical Chiral Nematic Liquid Crystal Phase of an Achiral Rigid Bent-Core Mesogen. *Phys. Rev. E.* 2014, *89*, 022506

Introduction

Nematic twist-bend phases represent a relatively new class of liquid crystals, first predicted by Meyer in 1973,[2] and experimentally seen in dimer systems since 2007.[3] In such phases, nematic order is characterized by oblique helicoid precession of the molecular director. Such helicoid precession of the director maintains an angle to the helical axis of the bulk, manifesting both twist and bend at a nanoscale level. Such an angle is not strictly orthogonal to the helix axis, differentiating these phases from well-known chiral nematic mesogens.

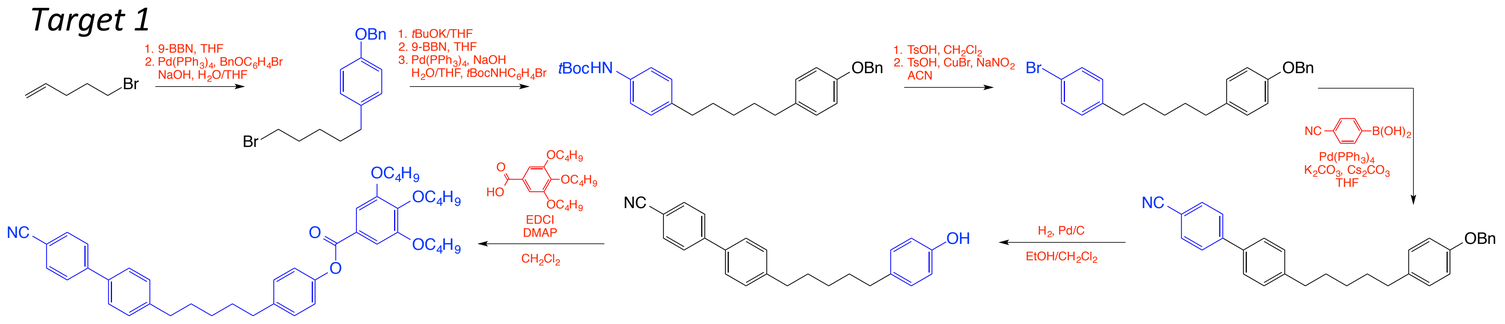
Basic Design:



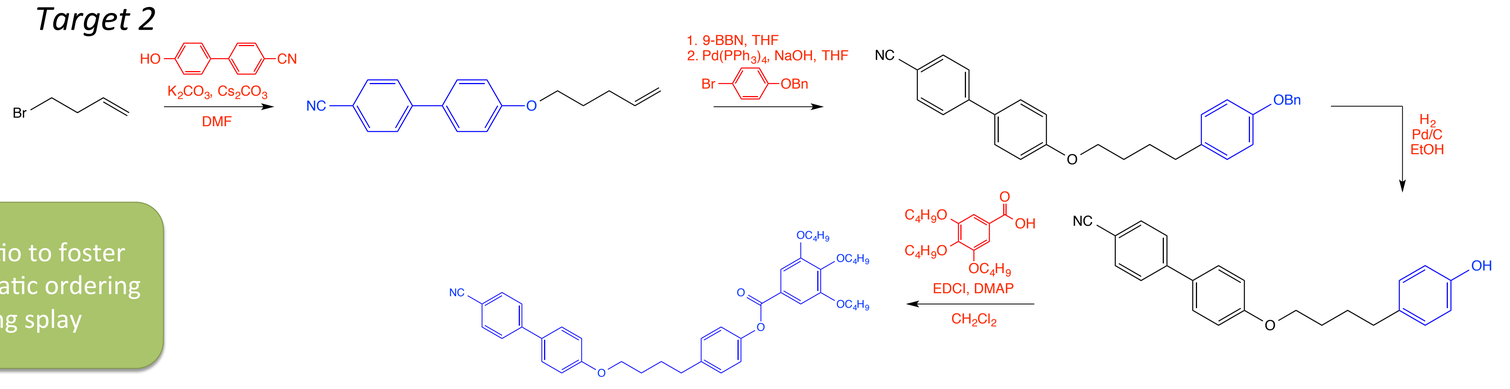
[2] Meyer, R. B. in Molecular Fluids. Les Houches Lectures, 1973. (eds. Balian, R. & Weill, G.) 271–343 (Gordon and Breach, 1976)
[3] Šepelj, M., Lesac, A., Baumeister, U., Diele, S., Nguyen, H.L., Bruce, D. Intercalated liquid-crystalline phases formed by symmetric dimers with an α,ω-diiminoalkylene spacer. *J. Mater. Chem.* 2007, 17, 1154–1165

Synthetic Approach

Target 1



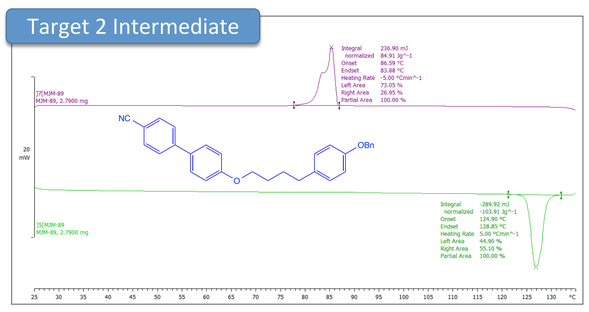
Target 2



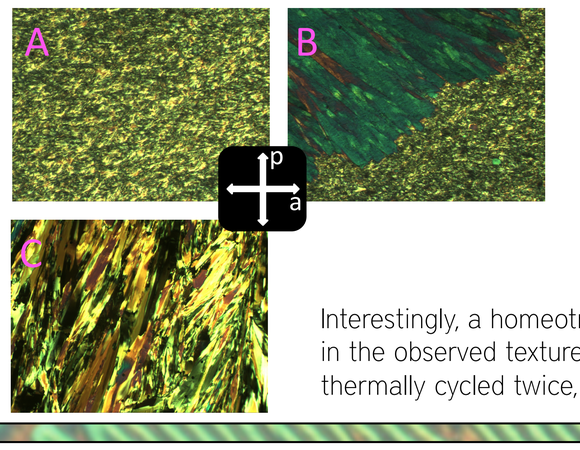
Results

Our variety of synthetic approaches has been widely successful, through the implementation of palladium catalysts, multiple Suzuki couplings, and a variety of substitution and elimination reactions. While *Target 1* is in the process of being synthesized, *Target 2* has been successfully synthesized. Interestingly, the synthetic intermediate for *Target 2* immediately following the B-alkyl Suzuki coupling to 4-benzyloxy bromobenzene exhibited a metastable mesogenic phase.

Target 2 Intermediate

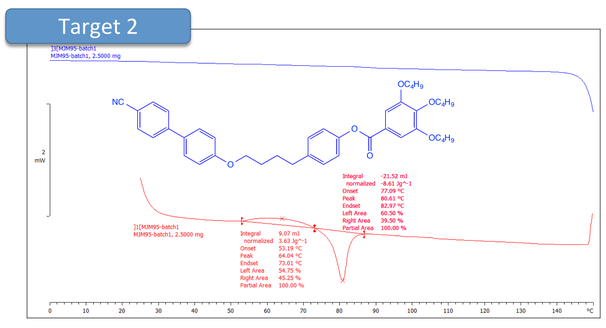


Differential scanning calorimetry of the *intermediate compound for Target 2* (*left*) shows a single monotropic phase appearing between approximately 86 and 83°C. Polarized light microscopy confirmed the presence of the phase on cooling, though there was a minor difference in the transition temperature from the unidentified mesogenic phase to the crystal.

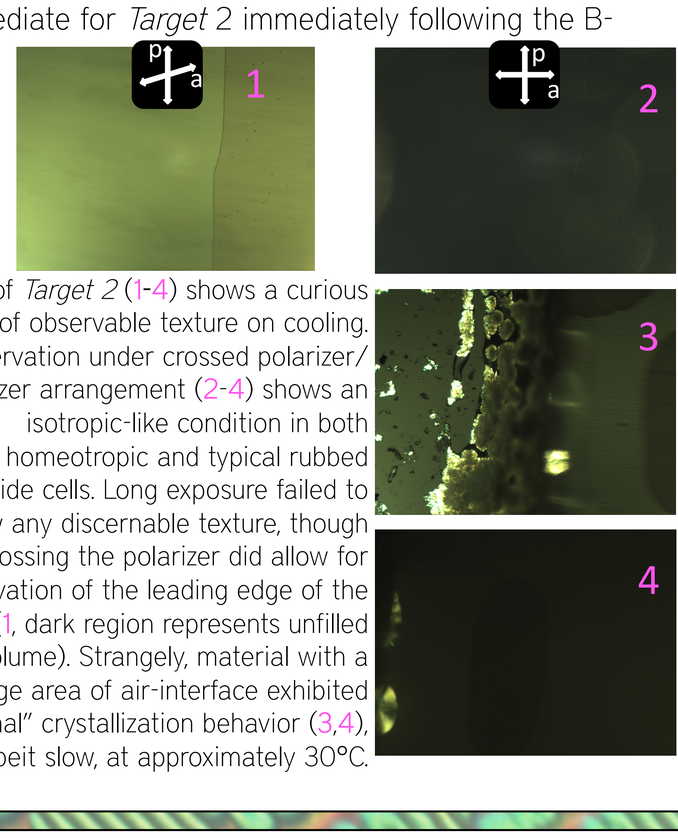


Microscopy performed in cells showed unexpected textures between 4µm planar (A,B) and 4µm homeotropic polyimide (C) cells. On cooling, an immediate texture showing lack of alignment was observed (A), though transition to a crystal-esque phase (B, *from upper left of image*) showed reasonable alignment of what is presumed to to be the incoming crystalline phase underneath. Interestingly, a homeotropically treated cell showed as little alignment in the observed texture as the planar alignment cells. Samples were thermally cycled twice, but yielded identical phases both times.

Target 2



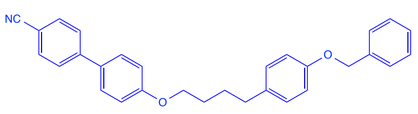
Differential scanning calorimetry of *Target 2* (*above*) shows a broad glass transition whose initial onset at 53°C immediately precedes a first-order transition at approximately 80°C. Polarized light microscopy confirmed the presence of the transition to the isotropic melt on heating. DSC results also show a curious lack of any first order transition to a crystal, down to 0°C. PLM observations also corroborate this result, though there is one minor discrepancy observed in the PLM (*see right*).



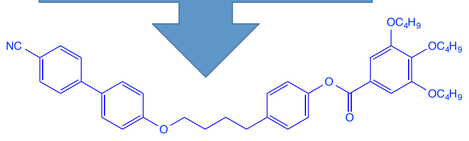
PLM of *Target 2* (1-4) shows a curious lack of observable texture on cooling. Observation under crossed polarizer/analyzer arrangement (2-4) shows an isotropic-like condition in both homeotropic and typical rubbed polyimide cells. Long exposure failed to show any discernable texture, though uncrossing the polarizer did allow for observation of the leading edge of the melt (1, dark region represents unfilled cell volume). Strangely, material with a large area of air-interface exhibited "normal" crystallization behavior (3,4), albeit slow, at approximately 30°C.

Discussion

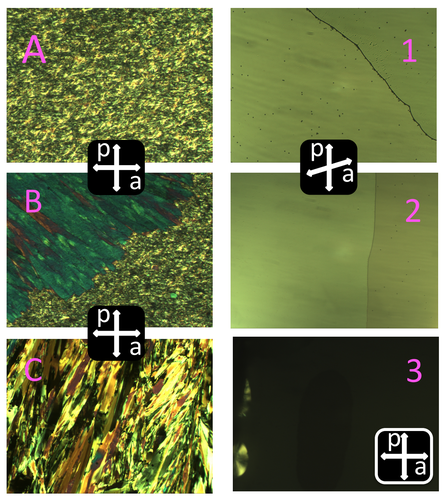
Initial results for *Target 2* and the characterized precursor yielded interesting results, raising a number of questions.



Increase in:
- Tail aspect ratio
- Lateral dipole moment
- Molecular weight



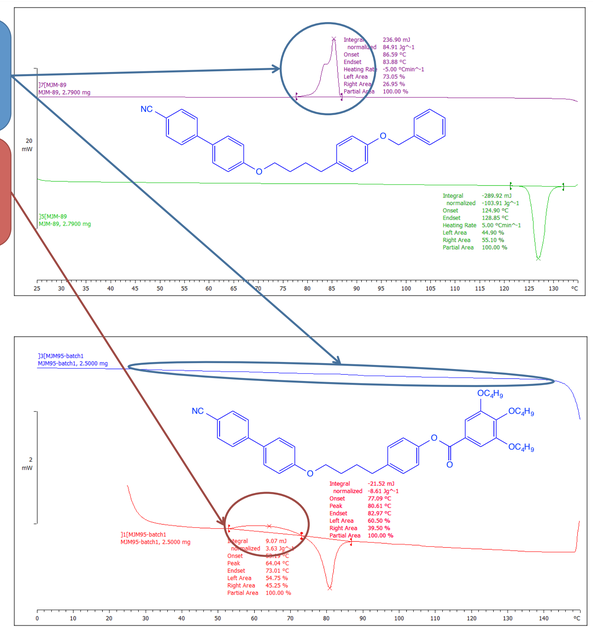
Addition of the trialkoxy gallate moiety appears to "kill" mesogenic behavior!
- PLM shows only isotropic texture
- DSC results are ambiguous



PLM images of the analog of *Target 2* (images A-C) under crossed polarizer/analyzer corroborate DSC data. A narrow phase is shown in images A and B, taken in planar alignment polyimide cells. In a homeotropic cell (C), a columnar-like texture is observed. This is in stark contrast to the PLM images of *Target 2*. In both a homeotropic cell (1) and planar cell (2) no texture is observed – the material appears to be isotropic for all purposes. It may be possible that the introduction of the gallate functional moiety is inducing the formation of an optically isotropic cubic phase that settles into a glass, but DSC data does not fully support this hypothesis as there is no first-order transition observed in the DSC through 0°C.

Exchange to the gallate eliminates the isotherm on cooling observed in the benzyl ether analog! It may be possible the isotropic liquid of the gallate exhibits an incredibly weak glass transition that is quite slow!

There is a clear glass transition preceding the transition to the isotropic liquid on heating for the gallate. The benzyl ether analog clearly does not show such a glass transition on heating. A potential metastable crystalline phase!



Future Work

It is clear that the addition of the gallate moiety has a significant impact on the mesomorphic behavior of the material. XRD spectroscopy is necessary to probe the apparent isotropic glass observed in the phase behavior of *Target 2*. Additionally, modification to eliminate the ester linkage may restore the observed phase in the benzyl precursor. Additional analogs that vary tail length of the gallate and variation of alkyl spacer length would be ideal for exploring this new structural space.

Acknowledgements

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