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A new class of high birefringence smectic C liquid crystals

3,3′-Difluorodiphenyldiacetylenes

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Ferroelectric smectic C* liquid crystals have been shown to exhibit high speed, multistate electro-optic switching, particularly when incorporated into the surface stabilized ferroelectric liquid crystal (SSFLC) light valve. Certain applications utilizing IR modulation, waveguide, and fibre-optic devices can benefit from a birefringence higher than the value of $\Delta n = 0{\cdot}15$ seen in typical FLC materials. By incorporating the highly conjugated diacetylene moiety into an FLC core, an increase in birefringence to greater than $\Delta n = 0{\cdot}3$ is achieved. Fluorination of the core induces a strong preference for the tilted smectic C phase as compared to the unfluorinated materials which typically show the nematic phase. The effect of different tail substitutions is examined in the 3,3′-difluorodiphenyldiacetylene system.

Although the number of uses for infrared (IR) light is constantly growing, the technology needed for high speed modulation of IR light is still in a state of infancy. Most IR modulators are mechanical in nature, although some work has been done using inherently slow nematic liquid crystal light valves.

One promising approach to this problem is a modulator based on the ferroelectric liquid crystal (FLC) device. In such a device, a thin layer of FLC material is placed between glass plates, and the optical properties of the layer are controlled by application of electric fields with high spatial resolution. Thus, ferroelectric liquid crystal (FLC) materials may provide a way to fabricate useful, fast IR modulators when incorporated into the surface stabilized ferroelectric liquid crystal (SSFLC) geometry. In an SSFLC cell, due to the presence of a ferroelectric polarization **P**, the orientation of the molecules in the FLC phase is strongly coupled to externally applied fields, affording a fast light valve with high contrast, bistability, a sharp threshold, low power requirements, and high spatial resolution.

Naturally, the characteristics of such devices depend to a large extent upon the FLC materials. FLCs form the material underpinning of a variety of opto-electronic devices possessing performance characteristics (combination of speed, contrast, bistability, and resolution) currently unachievable with any other materials [1]. The use of high birefringence FLC materials increases resolution limits and lowers voltage requirements by allowing the construction of thinner cells in such modulators.

The thickness of material used in the modulator must at minimum be the half-wave thickness of the material at the desired wavelength of light. In an SSFLC light

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modulator, the thickness of a half-wave plate is related to the birefringence by the equation

$$b=\frac{1}{2\Delta n\lambda},$$

where b is the material thickness, λ is the wavelength of light, and Δn is the birefringence of the material (the difference at a molecular level in the refractive index along the long and short axes). It can be seen from this equation, for example, that doubling the birefringence of the FLC mixture halves the thickness of the modulator.

This preliminary note reports on some of the properties of a new class of high birefringence liquid crystals-3,3′-difluorodiphenyldiacetylenes. A full paper detailing the physical and electro-optical properties will be published at a future date.

Examples of different classes of two ring FLCs are given in figure 1 and show the progression of Δn with conjugation length. It is interesting to note that the increased conjugation of the azoxy and MORA classes results in yellow coloured compounds, while the highly conjugated tolane or diacetylene classes are generally white solids. This illustrates how birefringence can be relatively uncoupled from dichroism associated with the molecule.

The diphenyldiacetylenes represent the highest birefringence of any class of two or three ring liquid crystalline materials. Although they are photo-labile [2] at wavelengths of less than 400 nm, their high birefringence and low viscosity make them attractive liquid crystalline candidates, particularly for IR applications where UV sensitivity is not a problem. The diacetylenes are therefore useful at visible wavelengths above 400 nm because, although they show a very high birefringence, they are colourless, white materials and show low absorption of light.

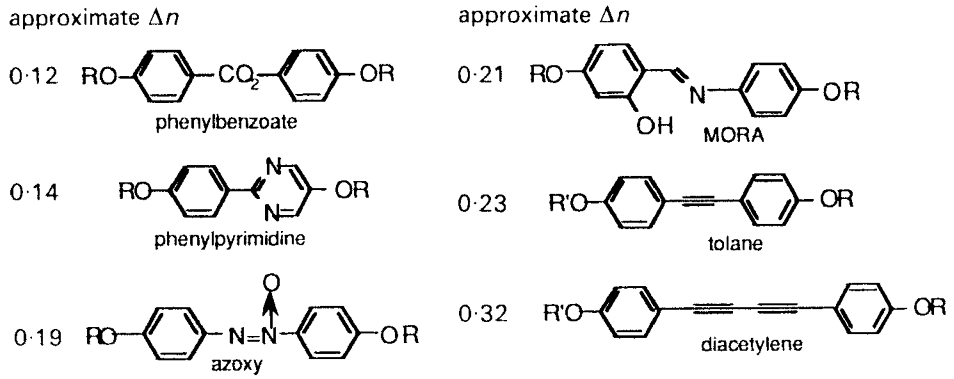
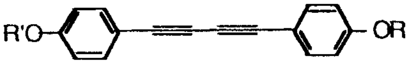


Figure 1. Comparison of the birefringence of some typical FLCs.

Diphenyldiacetylenes were first synthesized in the late 1950s by Eglington [3] and later explored by Wegner [4] in the early 1970s. Since then, much work has been devoted to the synthesis and polymerization of these interesting compounds into highly ordered conjugated polymers for use in non-linear optics applications [5].

The liquid crystalline diphenyldiacetylenes, of the general type shown below, synthesized and evaluated [6] at IBM in 1978, showed promise for use in the formulation of high birefringence nematic liquid crystalline mixtures. Both alkyl and alkoxyl tails were explored and both sets of materials afforded nematic phases.



These nematic compounds were later evaluated by Wu *et al.* [7], for use in IR applications. Most recently, Wu *et al.* [8] found that diacetylenes with unsymmetrical tails afford compounds with low melting-points and broad nematic-ranges. Simple

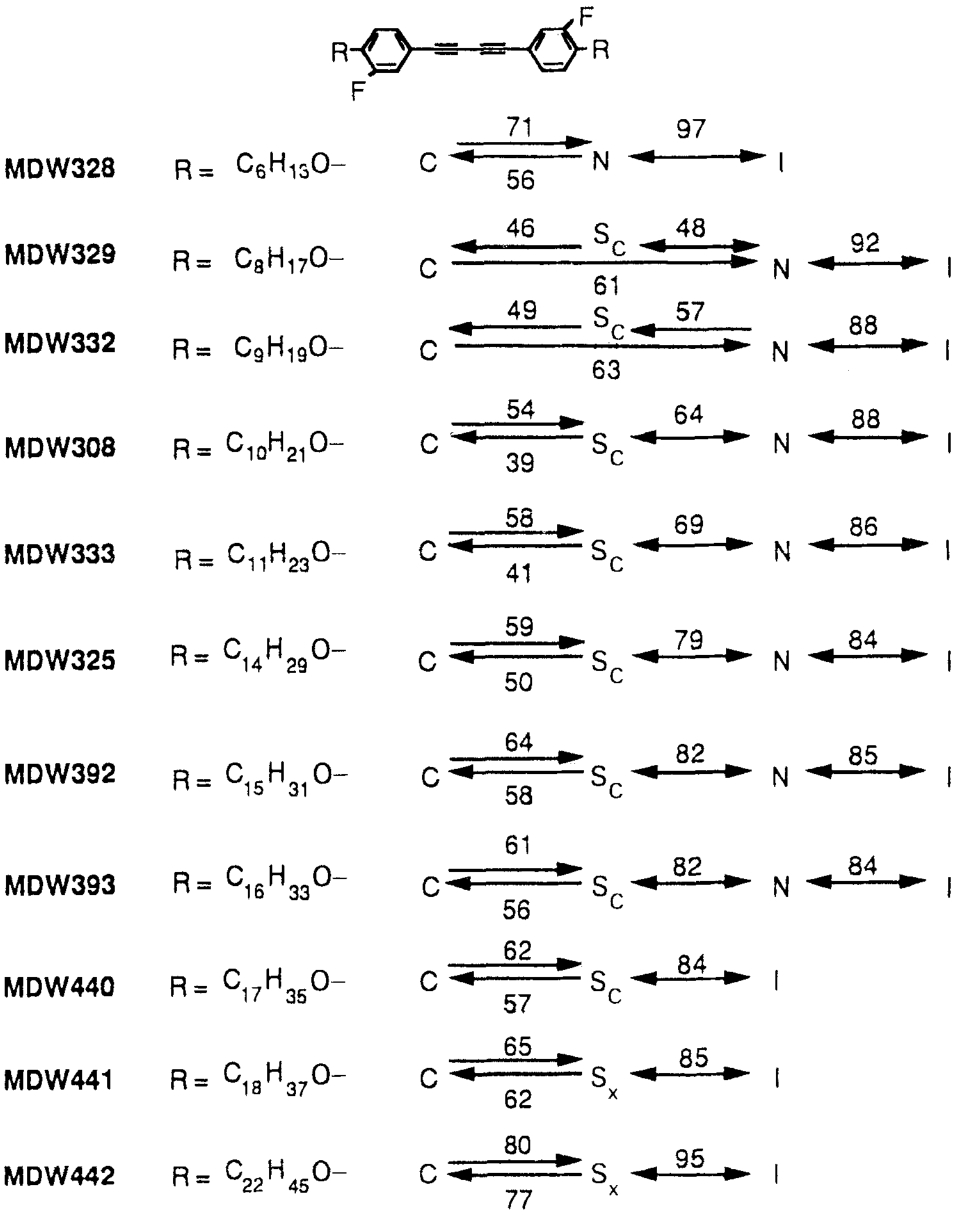


Figure 2. 4,4'-Di-*n*-alkoxy-3,3'-difluorodiphenyldiacetylenes: C = crystal, S_C = smectic C, S_x = ordered smectic, N = nematic, I = isotropic.

binary mixtures of these compounds afforded mixtures with nematic widths from 10 to 90°C. Several of the longer chain compounds in this class showed unidentified, narrow range smectic phases, typically several degrees wide. The existence of these smectic phases was intriguing and indicated the possibility of designing high birefringence smectic C materials by modifying the structure in some way.

Our observation that symmetrical *ortho*-fluorination of the rings afforded a broad enantiotropic smectic C phase in the C_{10} alkoxy analogue prompted us to explore further its homologues. Figure 2 highlights the trends that we found. This class of compounds typically showed a broad C phase with an overlying nematic phase. Every homologue from C_8 to C_{17} afforded a C phase and for homologues higher than C_9, the C phases were enantiotropic. Homologues with a chain length longer than C_{17} showed only higher order smectic phases.

The strong tendency of these compounds to show an N to smectic C or I to smectic C phase transition lends itself to applications benefiting from high tilt (45°), such as diffractive modulator-based devices using 0–π phase shift for beam steering.

Often, when a branched chain is substituted for an *n*-alkyl chain, the temperature of the existing transitions are lowered and broadened—a very attractive modification, if successful. The branched tail diacetylenes are shown in Figure 3, where the first material, **MDW 386** also shows the influence of a terminal double bond in the alkoxy group. While the decenyl tail afforded a smectic C material with a fairly low melting point, the saturated branched analogue **MDW 411** showed a complete suppression of the C phase, with only a monotropic nematic phase remaining.

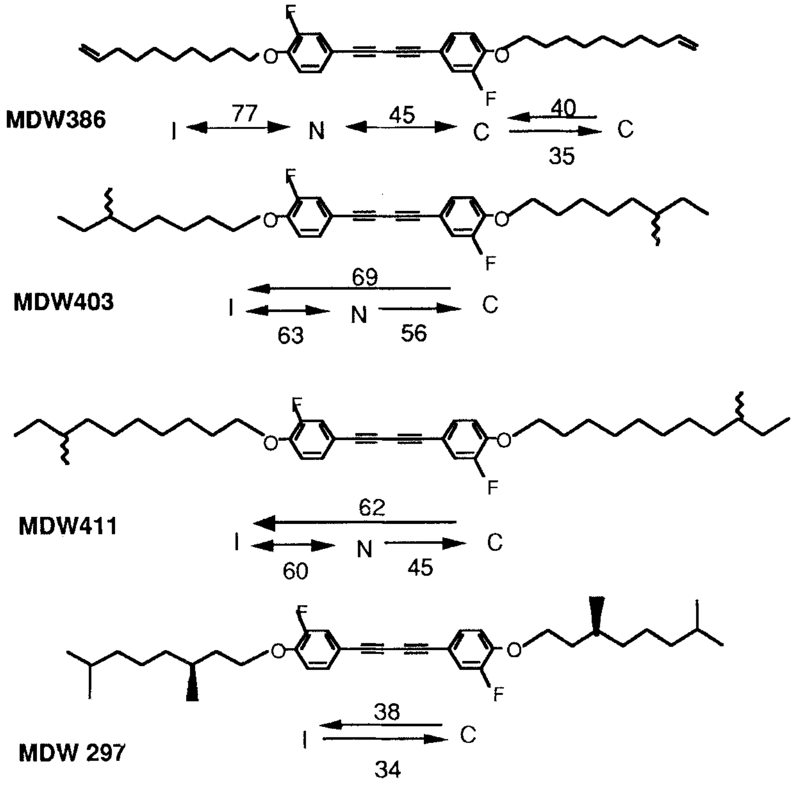


Figure 3. Branched alkoxy or alkenyloxy substituted 3,3′-difluorodiphenyldiacetylenes.

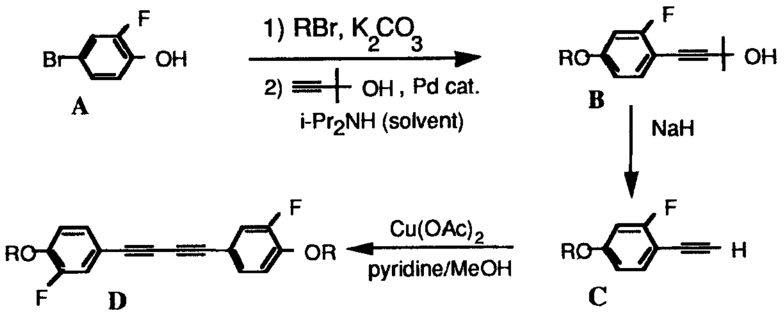


Figure 4. Synthetic route to the diphenyldiacetylenes.

Although the branched chain analogues showed no tilted smectic phases of their own, they can be used in small quantities to suppress melting points in mixtures.

A general synthesis of the 4,4′-dialkoxy-3,3′-difluorodiphenyldiacetylenes is outlines in figure 4. The starting material for the synthesis is the commercially available [9] 2-fluoro-4-bromophenol, **A**. This is first alkylated under basic conditions with the appropriate alkyl bromide and then allowed to react with 1,1-dimethylprop-2-yn-1-ol in the presence of palladium dichloride triphenylphosphinecopper (II) acetate [10] in boiling diisopropylamine, giving the protected acetylene **B**. The removal of the dimethylcarbinol group with the loss of acetone readily takes place upon treatment with sodium hydride in boiling toluene, yielding the acetylene **C**. This acetylene is dimerized using catalytic copper (II) acetate, affording the liquid crystalline 3,3′-difluorodiphenyldiacetylene **D**.

All compounds were synthesized by the described route (similar to that used by Grant [5]) with the final liquid crystal materials being purified by silica gel chromatography, followed by consecutive recrystallizations from hexane and acetonitrile.

In the search for high birefringence, thermodynamically stable, colourless materials showing the smectic C phase, we have introduced fluorine into the core of the well-known diphenyldiacetylene structure. This has resulted in a number of homologues which show broad temperature range, enantiotropic smectic C phases. The octyl and nonyl homologues show only monotropic C phases, while the decyl through heptadecyl homologues afford enantiotropic C phases as broad as 22°C. Chain lengths longer than seventeen carbons result in only higher order smectic phases.

In contrast to other liquid crystalline systems, branching of the chains totally suppresses the smectic C phase, affording only monotropic nematic phases in two cases and total suppression of all liquid crystalline phases in another case.

This new class of high birefringence materials should prove useful as smectic C hosts or as birefringence-enhancing dopants for ferroelectric liquid crystal-based applications such as IR shutters and optical cross bar switches that can benefit from a shorter optical path length.

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