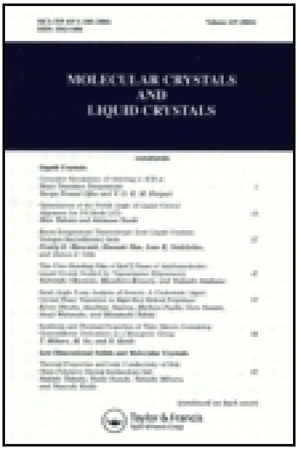

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Synthesis of New Photochromic Materials: Possible Multiplexing Devices?

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Synthesis of New Photochromic Materials: Possible Multiplexing Devices?

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Multistep syntheses of new photochromic systems derived from bis-thienylperfluorocyclopentenes are described. They are shown to be thermally stable, fatigue resistant and switch reversibly between colorless open forms and colored closed forms. The incredible stability of these reversible switches led to the attempts of incorporating thermotropic liquid crystalline nature. Polycatenar photochromic esters prepared seem to be mesogenic and thus may form the very first example of liquid crystals with Z-configuration.

Keywords: Photochromic; Liquid crystals; Z-configuration; Reversible switches

INTRODUCTION

Photochromic materials have attracted great attention as possible molecular switches over a decade now. Most of these materials are potential and unique candidates for optical data storage, optical switches and supramolecular devices. Azobenzens[1], fulgides[2], spiropyrans[3], dihydroazulenes[4], thioindigos[5] and diheteroaryl ethenes[6-19] are a few well-known and well-studied examples. Of these, diheteroaryl ethenes occupy a unique position because of its excellent thermal stability.

Bisthienylperfluorocylopentene, 1, stands out even among all the known diheteroaryl ethenes because of its thermal stability and its photo fatigue resistance[20-22]. They can undergo reversible switching between the colorless open form and colored closed forms on irradiation (FIGURE 1) for up to 10^4 cycles without any apparent decomposition, thus allowing its use in repeated data recording and data storage.

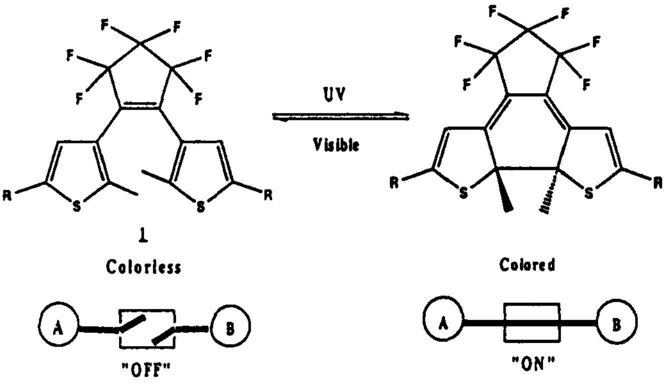


FIGURE 1. Bisthienylperfluorocyclopentenes, 1

The incredible stability of these reversible switches[23-25] has potential future applications and with the goal of realizing a few of them, the synthesis aimed at two new designs. One of them is to make 1 to exhibit liquid crystalline nature. Such combination would allow one to address two reversible changes independently among an array of states as shown, thus paving the way to a multiplexing system.

$$\begin{tikzcd}
\text{Open Form} \arrow[r, shift left, "h\nu_1"] \arrow[d, shift left] & \text{Closed Form} \arrow[l, shift left, "h\nu_2"] \arrow[d, shift left] \\
\text{LC}_1\text{-Open} \arrow[u, shift left, "T_1"] \arrow[r, shift left, "h\nu_1"] & \text{LC}_1\text{-Closed} \arrow[l, shift left, "h\nu_2"] \arrow[u, shift left, "T_2"']
\end{tikzcd}$$

It also offers the opportunity for wide variations of their properties using many independent external stimuli like magnetic and electric fields, heat and light. The intense color of the closed form allows a colored background for optical recording. The second design, which may form the building block for the first, is to make the dicarboxylic acid derivative of **1** for various supramolecular assemblies.

APPROACH TO MESOGENIC DESIGN

The molecular models as well as MMX minimized structures show the open form to be more flexible as expected, with anti-parallel conformer having lower energy than the parallel form (FIGURE 2). The closed form is more rigid with slight deviation from planarity at the sp^3 sites. Thus the closed form is no doubt has more or less the ideal backbone and is likely to be a liquid crystal with suitable mesogenic groups at 5,5' positions. In spite of the flexibility of the open form it seemed that it could exhibit at least some non-traditional lc character based on our previous work [26] on siloxane based twin dimers.

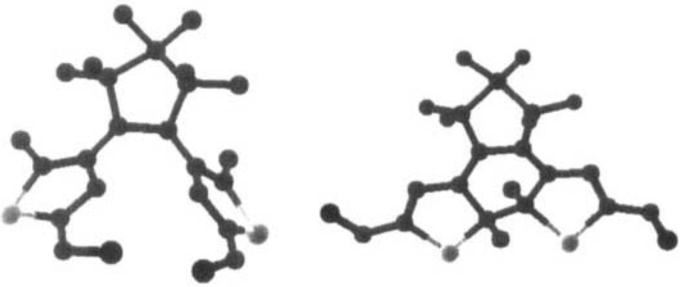
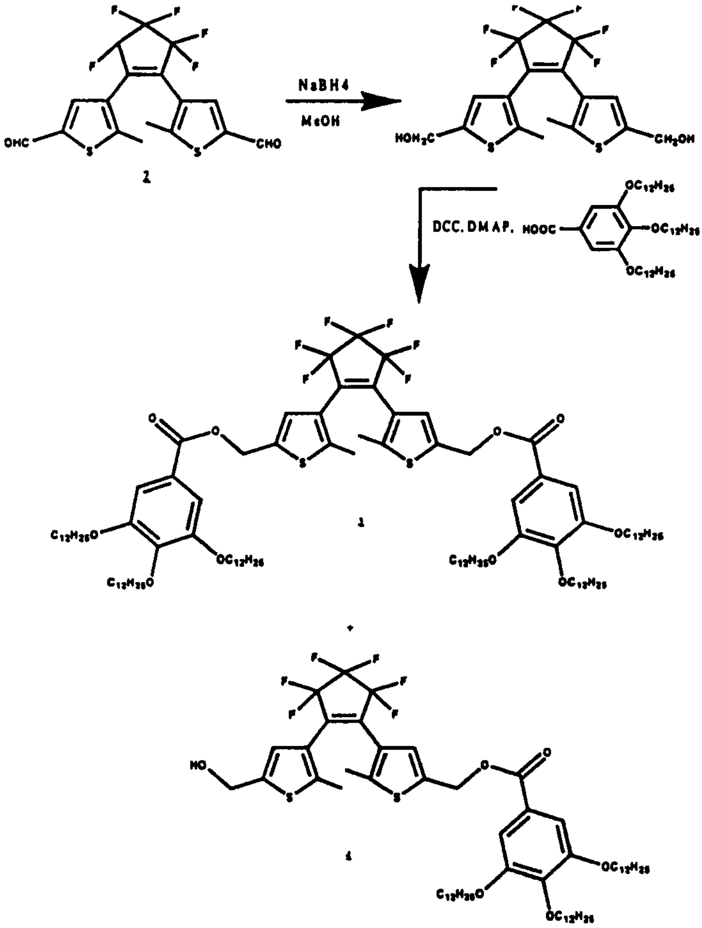


FIGURE 2. MMX optimized Structures of **1**
See Color Plate VIII at the back of this issue

With this rationale, the synthesis of the benzyl ester, **3** was undertaken from the photochromic aldehyde, **2**. The aldehyde was prepared by the reported procedure [23]. The ester was synthesized as shown in Scheme 1. The benzyl ester is a viscous liquid at RT and freezes at -5° C, indicating it is not a liquid crystal at or above RT. It should be noted that another photochromic liquid, the half ester 4 was also isolated as a byproduct and characterized well.

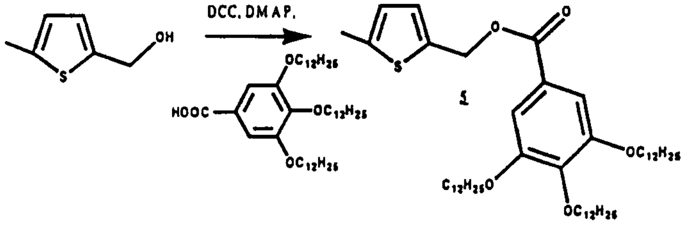


SCHEME 1. Synthesis of Photochromic Esters 3 and 4

Photochromic Behavior of 3 and 4

Both of them isomerize to the closed form upon irradiation with UV and switch back to the open form on exposure to visible (red) light. The closed form of 3 is dark red in color while that of 4 is dark purple. The rate of isomerization was followed by ^{1}H NMR and was followed by the intensities of thienyl and benzyl protons. Preliminary results show that the photo stationery state was reached after 3 hours of irradiation and at 65-70% isomerization with no decomposition. However, continuous irradiation for 4.5 h at 312 nm resulted in 10% decomposition of the ester. Irradiation by visible light for 4 h reverts it completely back to the open form. The half ester shows a very similar behavior.

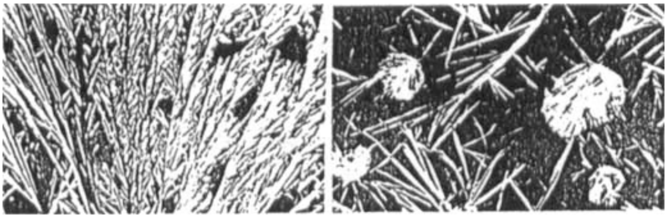
Benzyl esters are reported [27] to undergo photochemical decomposition. To verify this fact, a model ester, 5 was prepared (SCHEME 2) from 2-thienylmethanol; it shows a similar photolabile behavior on UV irradiation.



SCHEME 2. Synthesis of Model Ester 5

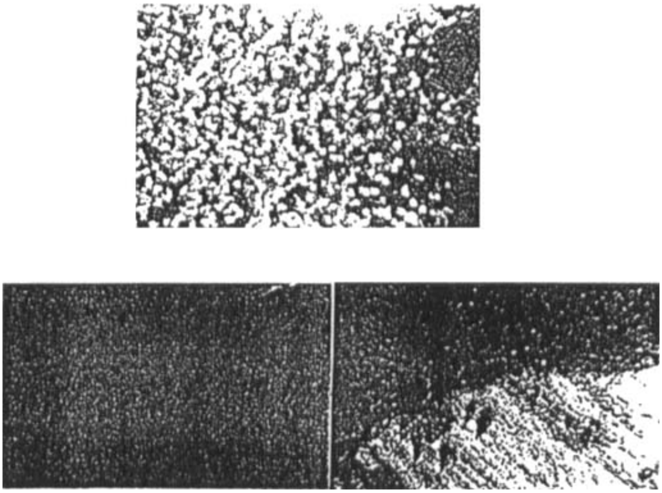
Mesogenic Behavior of 3, 4 and 5

The mesogenic nature was studied by DSC and by microcopy. The model ester 5 shows a transition at 28.2°C just before the clearing point at 39.6°C. The same transition was not observed during the cooling cycle. Microscopic observations show textural change confirming a short range unidentified crystalline smectic phase (Plate 1-2)



PLATES 1-2/ LC Textures of Model Ester **5**
See Colors Plates IX and X at the back of this issue

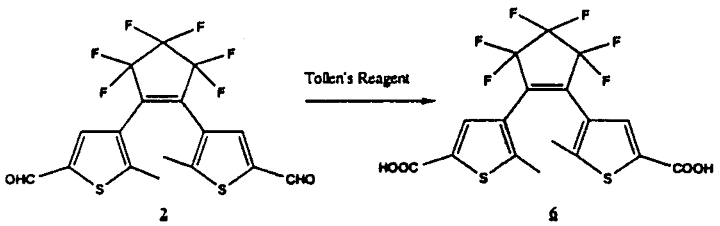
DSC shows a single transition for the open form of **4** and **5** both on heating and cooling cycles. Microscopic observation of **4** suggests that it may have a nematic transition (Plate 3). DSC of the closed form of **4** shows two major transitions, both on heating and cooling cycles Microscopic observations show a nice uniform red color and lc textures (Plates 4-5). Further work is being continued to identify the phases.



PLATES 3-5. LC Textures of **4** – Open Form (Top, Plate 3); Closed Form (Bottom, Plates 4-5)
See Colors Plates XI, XII and XIII at the back of this issue

SYNTHESIS OF PHOTOCHROMIC ACID, 6

Since the benzyl ester is somewhat photolabile the photochromic acid was synthesized by the Ag^+ oxidation of **2** in almost 99% yield (SCHEME 3). The acid switches reversibly from colorless to purplish blue form and reaches photo stationary state at 85% isomerization. Visible Irradiation isomerizes it to the open form within 4-5 hours.



SCHEME 3. Synthesis of Photochromic Acid 6

X-ray crystal structure analysis of the acid shows it to be a hydrogen-bonded network (FIGURE 3) with itself and with solvent molecule.

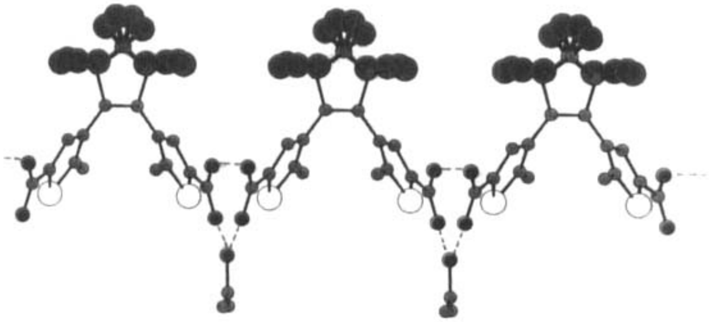
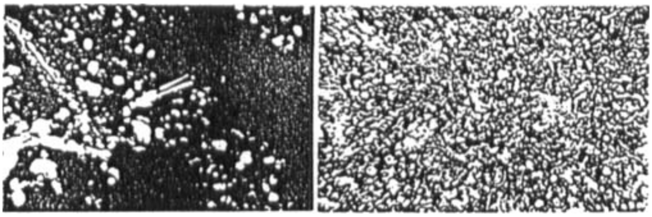


FIGURE 3. Hydrogen Bonded Network of 6 with solvent. The crystals composed of a 1:1 mixture of two conformers of ring as shown See Color Plate XIVat the back of this issue

Mesogenic Behavior of 6

DSC observations of the open isomer show clearly more than two transitions and microscopy also confirms distinct texture changes suggesting liquid crystalline transitions (Plates 6-7). The identities of these phases are yet to be determined. The same is true of the closed dark purple form. The microscopic observations are yet to be carried out on the closed form.



PLATES 6-7. LC Textures of **6**
See Colors Plates XV and XVI at the back of this issue

FUTURE DIRECTIONS

A number of microscopic observations made on the precursors suggest that these molecules show some unusual behavior either because of the perfluorocycloalkene ring or due to the herterocycle present. Current efforts are directed towards preparing model esters from thiophene carboxylic acids and from **6**. In summary, our preliminary work provides guidelines and insight to better design for the synthesis of photochromic–liquid crystalline materials. These materials, once synthesized, should pave the way to a wide variety of applications in optical recording and storage and as multiplexing devices.

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