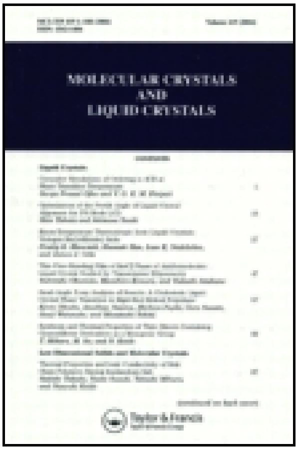

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New Spiropyrans and Spirooxazines Compounds With one or two Thiophene Nuclei. Applications to Anticopying Protection Materials

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NEW SPIROPYRANS AND SPIROOXAZINES COMPOUNDS WITH ONE OR TWO THIOPHENE NUCLEI. APPLICATIONS TO ANTICOPYING PROTECTION MATERIALS.

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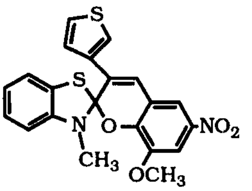
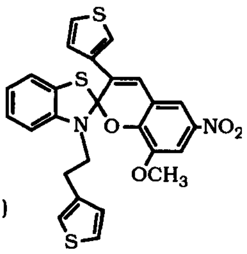
Abstract The strategy of synthesis of new thiophene-substituted spiroheterocyclic photochromic structures, in spiropyran or spirooxazine series is described. The polymerization of thiophene entity give interesting semi-conductor systems. Such molecular materials prevent the reproduction of documents and could be useful in other applications such as fast optical switches.

The observation of photochromism in spiro[indoline-benzopyrans] dates back to 1952[1], since then an enormous amount of work has been devoted to synthesizing new compounds with relevant industrial interest[2]. Following previous studies in this area, we have synthesized a variety of thiophene-substituted spiropyrans and spirooxazines. We report the synthesis and spectrokinetic properties of spiro[benzothiazoline-benzopyrans] (I) and (II), spiro[indoline-benzopyran] (III) and spiro[indoline-naphthoxazine] (IV), including one or two thiophene entities, polymerisable into a polythiophene matrix[3].

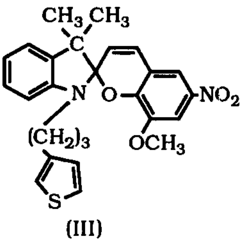
The thiophene nuclei can be directly conjugated to the " π " system of the spiroheterocyclic molecule or isolated by a carbon chain containing two or three carbon atoms. This flexible spacer allows to prepare oligomers under oxidative catalyst[4].



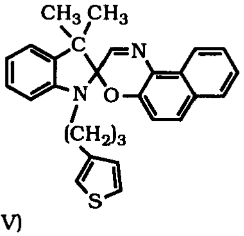
(I)



(II)



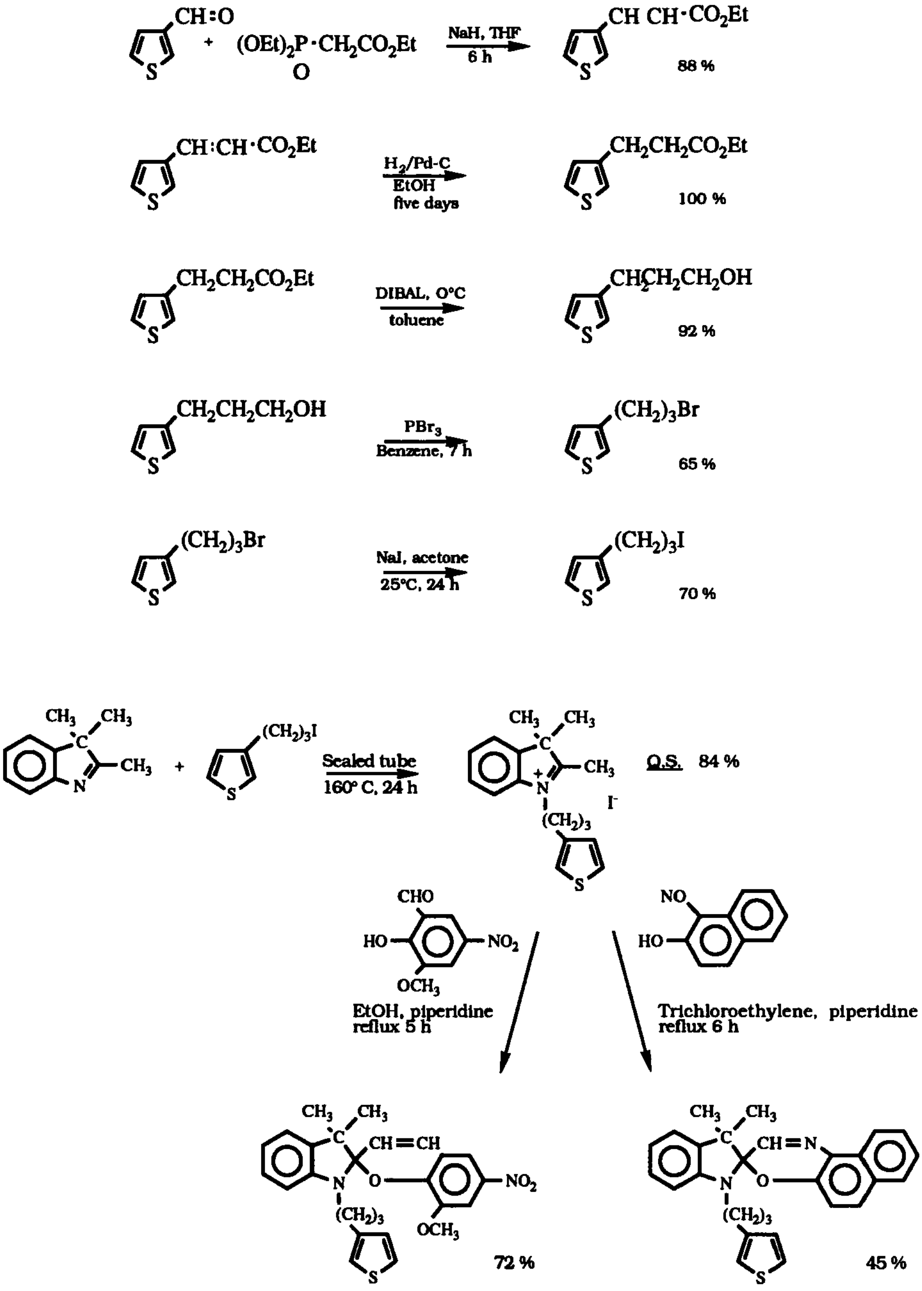
(III)



(IV)

SYNTHESIS

The compounds (III) and (IV) were prepared as follows :



SPECTROKINETIC PARAMETERS

We report in Table I the maxima absorption wavelenght of the photomerocyanine, the thermal bleaching kinetic constant and the "colorability" measured in toluene at 298K. Concentrations used were 2.5 10^{-5}M. Voltage (E=6 kV).

TABLE I Spectrokinetic data for some spiro derivatives.

	(I)	(II)	(III)	(IV)
λ_{max} (nm)	630	630	605	(554) 593
k_{Δ} (s^{-1})	4 - 5	7 - 8	2.3 10^{-2}	58 10^{-2}
A_0	0.12	0.07	2.7	1

Conceivably, the presence of a thiophene entity linked on a nitrogen atom provokes slight changes of spectrokinetic parameters. The very low rate constants of thermal ring closure of the compounds (III) and (IV) make them interesting candidates for practical applications.

APPLICATIONS

Attempts of polymerisation of these monomer molecules have been underdone, aiming at the realization of conjugated polythiophene chains, well known for their charge transport properties, and bearing also spiropyran units as pendant groups. However, although using various experimental conditions for the polymerization of the thiophene units, no conjugated polythiophene chain could be obtained.

The large steric hindrance originating from the spiropyran units can be put forward for explaining the absence of polymerization of the thiophene units. Nevertheless, in order to determine if the photochromic ring opening of the spiropyran units could be sensitized through the excited or charged states of the thiophene moieties, thin polymethylmetacrylate films containing both a spiropyran molecule and a conjugated polythiophene have been analyzed.

First experiments have shown that the excitation of polythiophene in its intra band states allowed, through intermolecular transfer to spiropyran, the ring opening of the spiropyran, leading to the corresponding merocyanine which has been characterized spectroscopically. These results confirm that an intramolecular transfer between an excited conjugated chain and a spiropyran group grafted as pendant group on this chain can be achieved.

Work is actually on progress for the synthesis of such spiropyran-functionalized polythiophenes.

These materials prevent the reproduction of documents and could be useful in other applications such as fast optical switches.

ACKNOWLEDGMENT

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