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Methylenepyran based dipolar and quadrupolar dyes: synthesis, electrochemical and photochemical properties

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ABSTRACT

This paper presents the synthesis of a series of push–pull and quadrupolar π-conjugated structures incorporating pro-aromatic methylenepyran electron-donor groups and various electron-attracting groups. Some of the methylenepyran derivatives were oxidized by I_2 to give, after reduction by $Na_2S_2O_3$, bismethylenepyran compounds via successive steps.
The electrochemical redox properties of methylenepyrans **5**–**9** and extended bismethylenepyrans **10**, **14**, and **15** determined by cyclic voltammetry indicate the formation of redox bistable systems with high bistability. Oxidation of the dimers obtained from **5** to **9** was also described. All compounds are colored and slightly fluorescent (except some bismethylenepyran derivatives). Some compound second-order nonlinear optical properties were investigated, and large positive values of $\mu\beta$ were obtained. A positive dimer effect was also observed for bispyran derivatives.

1. Introduction

Donor–acceptor π-conjugated (D–π–A) materials with both electron-donating and electron-accepting groups linked by a π-conjugated bridge have been extensively studied during the past decades due to their useful applications as sensitizers for dye-sensitized solar-cells (DSSCs),[1] emitters of organic light emitting diodes (OLEDs),[2] and various fluorescence sensors.[3]

Push–pull molecules with large delocalized π-electron systems are also typical second and third order nonlinear optic (NLO) chromophores.[4] Quadrupolar D–π–A–π–D structures also exhibit third order NLO properties. Second-order NLO materials have found applications in green lasers obtained from red sources through frequency doubling, in second-harmonic generation microscopy or in terahertz wave generation.[5] Third order NLO, in particular two-photon absorption (TPA) materials have also attracted considerable attention due to their applications in photodynamic therapy, confocal microscopy, optical power limiting and 3D data storage, and microfabrication.[6] Unlike inorganic materials, organic compounds used for NLO applications offer several advantages, such as easy syntheses, well-defined structure, easily tunable properties, and large optical nonlinearities and responses. γ-Methylenepyrans are versatile six-membered heterocycles with a pro-aromatic electron-donor character. It is well-known that chromophores incorporating aromatic subunits display lower β values than the corresponding polyenes of the same conjugation length, since their ground states are usually dominated by neutral, aromatic forms that lose resonance energy on charge separation.[7] One way to circumvent this drawback consists of incorporating a molecular fragment whose aromaticity will increase upon charge transfer. In this context, γ-methylenepyrans, which acquire the aromatic character of pyrylium upon internal charge transfer, are particularly attracting as donor part in push–pull structures. The use of such molecular fragments in the structure of NLO chromophores has already been described in the literature.[8] Moreover, π-conjugated structures incorporating γ-methylenepyran building blocks have also been described as interesting redox systems.[9] In particular, it has been described that oxidative dimerization of methylenepyrans bearing exocyclic ferrocenyl groups leads to the formation of bispyrilium salts via a radical cation intermediate. Subsequent deprotonation led to extended diferrocenylbispyran, which were then oxidized into unsaturated bispyrilium salts.[10]

On the other hand, diazines are six-membered aromatics with two nitrogen atoms. Three different structures can be distinguished based on the relative position of the nitrogen atoms: pyridazine (1,2-diazine), pyrimidine (1,3-diazine), and pyrazine (1,4-diazine). Diazines are very attractive electron accepting building blocks for

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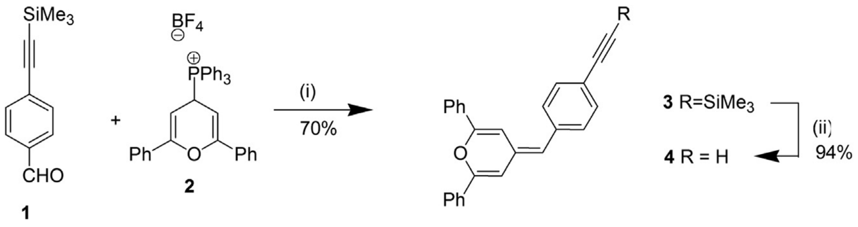
the synthesis of push–pull, quadrupolar, and octupolar structures. Such structures exhibit high fluorescence due to internal charge transfer, important TPA properties and can be used as dyes for DSSCs.[11–13] The possibility to protonate, form hydrogen bonds, and chelate the diazine rings also present additional advantages.

Recently, some of us have described the NLO properties of two pyrimidine γ-methylenepyran derivatives.[14] In the present article, we describe the synthesis, the electrochemical and the optical properties of a series of push–pull, bispush–pull, and quadrupolar structures with an extended π-conjugated core incorporating γ-methylenepyrans as electron-donating parts and various electron-accepting groups, in particular diazine rings.

2. Results and discussion

2.1. Synthesis

The key intermediate for synthesis of push–pull structures is alkyne **4**. This compound can be obtained in two steps from 4-trimethylsilylethynyl-benzaldehyde **1** and phosphonium salt **2**[15] (Scheme 1). The first step is a Wittig reaction[16] leading to intermediate **3** with good yield and the second step consists of the deprotection of the trimethylsilyl group with quasi-quantitative yield.



Scheme 1. Reagents and conditions: (i) *n*-BuLi, THF, −78 °C→rt, 2 h (ii) K_2CO_3, $MeOH/CH_2Cl_2$, rt, overnight.

The intermediate **4** can be involved in a copper/palladium-catalyzed Sonogashira cross-coupling reaction with a variety of substituted bromobenzenes (Scheme 2).[17] Compounds **5**–**8** have been obtained in moderate to good yield. It should be noted that a small proportion of dimer **10** is systematically formed during the reaction, even when using $Pd(PPh_3)_4$ instead of $Pd(PPh_3)_2Cl_2$ as palladium catalyst. Aldehyde **8** can be used in a Knoevenagel condensation reaction with malononitrile leading to dicyano derivative **9**.

It has been reported that alkynyldiazines can be obtained from iododiazines by Sonogashira cross-coupling under mild synthetic conditions with good yield.[18] Similar conditions were used to synthesize building block **4** and a variety of monoiodo and diiododiazines leading to push–pull structures **11**–**13** and quadrupolar compounds **14**, **15**, with moderate to good yield (Scheme 3).

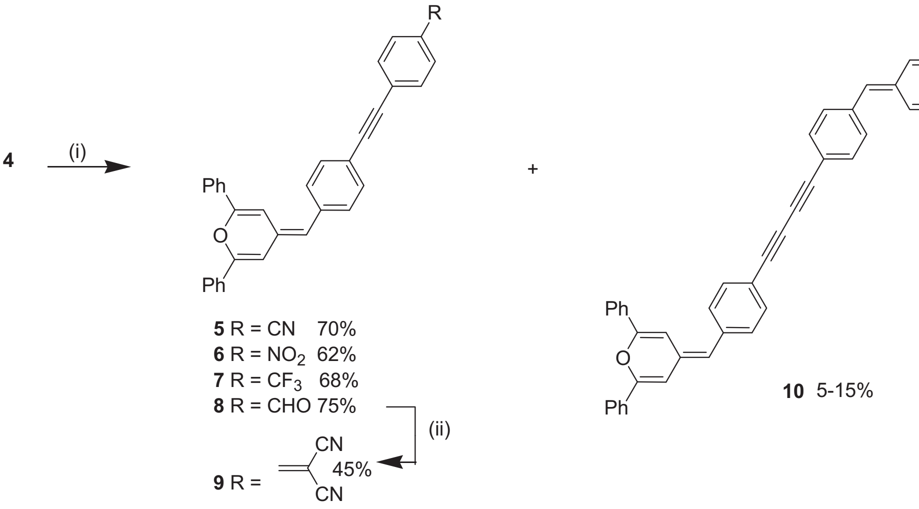
Dithiafulvenes and methylenepyrans have been reported to dimerize in the presence of oxidant by oxidative coupling via a radical cation intermediate.[10b,19] This method was used with some of the methylenepyrans described (compounds **5**–**9**) using diiode as oxidant (Scheme 4). Addition of a reducing agent ($Na_2S_2O_3$) to the reaction mixture gave bismethylenepyran coupling products **16**–**20**, with moderate yield. This suggests that under such oxidative conditions, the formation of the dimers proceeds from the following successive steps: (1) dimerization of compounds **5**–**9** via a radical cation intermediate leading to bispyrylium salts. (2) Deprotonation of the salts to give bismethylenepyrans **16**–**20**. (3) Oxidation of the neutral dimers to dicationic pyrylium species, which were then reduced by $Na_2S_2O_3$ to give bismethylenepyrans **16**–**20**.

All new compounds were soluble in THF, chloroform, and dichloromethane and were characterized using ^1H and ^{13}C NMR and high-resolution mass analysis. These materials were also perfectly stable in the solid state and did not require special storage conditions.

2.2. Electrochemical studies

The redox properties of the series of pyrans **5**–**9** and **11**–**13**, extended bispyrans **10**, **14**, and **15**, and diarylacetylene bispyran **16**–**20** (Table 1 and Fig. 1) were investigated by cyclic voltammetry in CH_2Cl_2 in the presence of NBu_4BF_4 as supporting electrolyte. All potentials are given versus $FeCp_2^+/FeCp_2$ couple.

The cyclic voltammogram of **9** (Fig. 1a) shows an irreversible anodic peak at 0.31 V and, on the reverse scan, an irreversible



Scheme 2. Reagents and conditions: (i) bromobenzene derivative, $Pd(PPh_3)_2Cl_2$, CuI, THF, NH*i*Pr_2, 60 °C, overnight (ii) 2 equiv malononitrile, AcOH/AcONa, benzene, reflux, 5 h.