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Syntheses of four new pyridinium phenolates with caged phenolate functionalities as chromophores for quadratic optics

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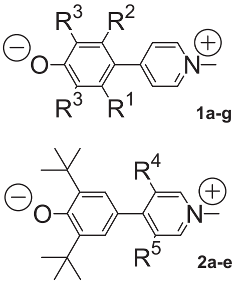
ABSTRACT

Semi-empirical calculations as well as our preliminary studies indicate an increase of the nonlinear response of pyridinium phenolates with the raise of their interplanar angle. Unfortunately, the tendency of previously synthesized zwitterionic compounds to form aggregates prevents their use in electro-optical devices. In order to understand the process of aggregation and to circumvent it, the syntheses of new pyridinium phenolates bearing alkyl chains of various length, caging the phenolate functionality, have been achieved and are described herein.

1. Introduction

Pyridinium phenolates have shown to be model push–pull molecules with large nonlinear optical properties. These are twisted intramolecular charge-transfer molecules, that is, in other word, tictoïds. They are characterized by a large permanent dipole moment in the electronic ground state. Semi-empirical calculations[1–4] as well as previous work,[5] indicated that increasing the interplanar angle between the two aromatic rings could enhance their NLO properties.

Since a few years our objective is the preparation of pyridinium phenolates with various interplanar angles and bearing (or not) protecting groups at *ortho* position of the phenolate functionality (Scheme 1). The medium-term purpose of our work is the selection of the most promising compound with respect to its high hyperpolarisability and solubility in order to dope polymers for the development of promising electro-optical materials.



	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
R^1	H	H	Me	Et	*i*Pr	H	Me
R^2	H	Me	Me	Et	*i*Pr	H	Me
R^3	H	H	H	H	H	Me	Me

	2a	**2b**	**2c**	**2d**	**2e**
R^4	H	H	Me	Et	*i*Pr
R^5	H	Me	Me	Et	*i*Pr

Scheme 1. Zwitterionic compounds previously synthesized.[6,7]

Until now, two series of pyridinium phenolates, sterically hindered at the *ortho* position of the intercyclic bond, have been synthesized. Unfortunately, the low solubilities of compounds **1a**–**e** made their NLO characterization difficult.[8] Much more reliable results were obtained with compounds **2a**–**e** in which two *tert*-butyl groups are anchored at the *ortho* positions of the phenolate ring.[5] Actually, *tert*-butyl groups are known to notably reduce the formation of aggregates. In addition, the enhancement of the molecular mass led to a better solubility of the corresponding tictoïds in organic solvents. Unfortunately, the solubilities obtained are not yet sufficient and aggregation is still a persistent phenomenon, which precludes a potential use in integrated optical devises. In order to circumvent these two main drawbacks and to understand the process of aggregation better, aliphatic chains of various lengths were linked, via ether functions, at both *ortho* positions of the phenolate ring. A restricted torsion angle was obtained by introduction of two methyl groups at the *meta* position of the pyridine ring, leading to a twist angle of about 45° as for **2c**.[5] The

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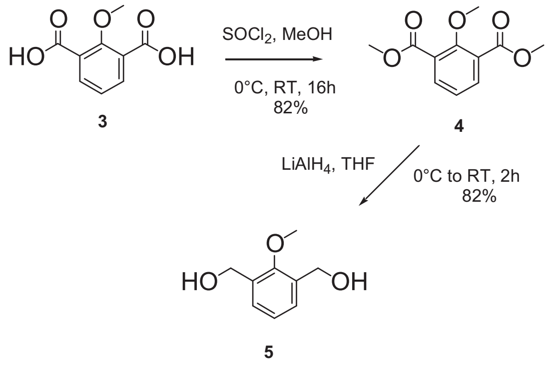
synthesis of four new betaine chromophores having these last mentioned characteristics is described herein.

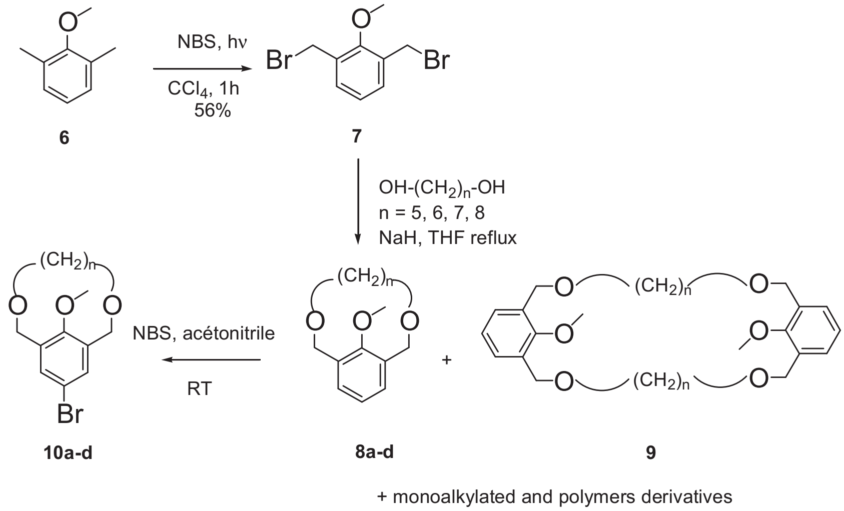
2. Results and discussion

2.1. Syntheses of bromocyclophanes 10a–d

In a first approach, **5** was readily synthesized in two steps from the known 2-methoxy*iso*-phthalic acid **3**.[9] Compound **3** was first converted into its dimethylester **4** by reaction with $SOCl_2$ in anhydrous MeOH (Scheme 2).[10] Then, reduction with $LiAlH_4$ afforded **5** in 67% total yield from diacid **3**.



Scheme 2. Preparation of **5**.



Scheme 3. Preparation of **8a–d** and **10a–d** (n = 5, 6, 7, 8).

A condensation between 1,5-dibromopentane and the bis(hydroxymethyl) compound **5** was then attempted under high-dilution condition. Unfortunately, using *t*-BuOK as base, as well as in THF and in DMF, the reaction led to a complete decay of **5**. On the contrary, in 1,4-dioxane, or in the presence of NaH in THF, no reaction occurred and **5** was recovered quantitatively.

We therefore decided to invert the reactive functionalities of the two partners as described in the literature for the syntheses of 2-methoxy-1,3-xylyl crown compounds.[11–14] The known 2,6-dimethylanisole **6** was therefore brominated using NBS under irradiation, via a radical substitution, to obtain bis(bromomethyl) anisole **7** in 56% yield.

Condensation of 2,6-bis(bromomethyl)anisole with alkanes-1,*n*-diols (n=5–8) of various lengths, conducted in the presence of sodium hydride in anhydrous THF at reflux and under high-dilution conditions, afforded the desired cyclophanes **8a–d**. Despite a meticulous optimisation of the reaction conditions, the cyclophanes were obtained mixed with by-products (i.e., 25% of various monosubstituted anisoles and about 20% of dimer **9**) (Scheme 3). Cyclophanes **8a–d** were subsequently purified by flash chromatography and recovered in yields ranged between 15 and 43% (Table 1). Finally, they were readily brominated into 4-bromoanisoles **10a–d**, using NBS.

2.2. Synthesis of boronic ester 12

The preparation of the boronic ester **12** from the known 4-bromo-3,5-dimethylpyridine **11**[7] was easily performed, in 61% yield, via a classical bromide/lithium exchange followed by treatment with tributylborate and then pinacol.

2.3. Suzuki–Miyaura coupling reaction–deprotection–quaternisation

The following three steps, namely the cross-coupling reaction followed by deprotection and quaternisation, were performed under the same conditions as previously described for the syntheses of **1a–e** and **2a–e**.[6,7] The Suzuki–Miyaura coupling reaction of **11a–d** with boronic ester **12** afforded the 4-pyridinylanisoles **13a–d** in good to excellent yields (from 75 to 82%), using our usual conditions [$Pd(PPh_3)_4$ as catalyst and Cs_2CO_3 as base in anhydrous THF] (Table 1, Scheme 4). Then, the phenol functions were deprotected, in DMF, at 100 °C, using sodium ethanethiolate, pre-

Table 1
Yields leading from **7** to **16a–d**

	n	Cyclisation			Bromination		Suzuki–Miyaura coupling yield/%	
		Time/h	Yield/%		Time/h	Yield/%		
8a	5	96	15	**10a**	8	85	**13a**	85
8b	6	96	25	**10b**	8	95	**13b**	75
8c	7	48	38	**10c**	1	88	**13c**	80
8d	8	48	43	**10d**	1	90	**13d**	85

Deprotection yield/%		Quaternisation yield/%		Deprotonation yield/%	
14a	66	**15a**	70	**16a**	60
14b	65	**15b**	80	**16b**	65