

## THE ANODIC TRIMERIZATION OF AROMATIC ORTHODIETHERS : NEW DEVELOPMENTS

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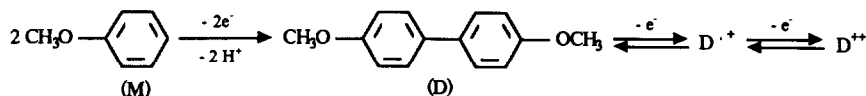
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**Summary :** While the anodic trimerization of veratrole (leading to hexamethoxytriphenylene) is now a very well known reaction, developments concerning either mixed electrolysis (mixture of two orthodiethers) and/or oxidation of dissymmetrical substrates have not been conducted so far. The presented method, often specific, allows the synthesis of a new palette of liquid crystal precursors.

### INTRODUCTION

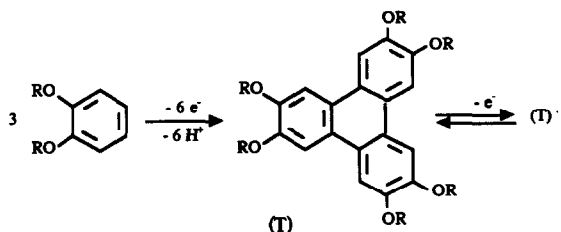
The anodic oxidation of phenol ethers is now a well described reaction. Intermediate cation<sup>1</sup> radicals are very reactive transients. They can be deprotonated by reaction with bases or also react with nucleophiles such as water. In order to conduct the dimerization of aromatic ethers (formation of an aromatic-aromatic linkage), a large palette of non nucleophilic media can be used<sup>2</sup> (dichloromethane, nitrobenzene, liquid sulphur dioxide, fluorosulfonic acid, trifluoroacetic acid or molten salts such as aluminium trichloride). Especially, it was shown by Parker<sup>3</sup> that solvent mixtures like dichloromethane and trifluoroacetic acid exhibit a stabilizing effect on cation-radicals by inhibiting more or less the nucleophilic action of residual water. As a matter of fact the presence of trifluoroacetic acid often appears to be absolutely necessary if good yields of coupling are to be obtained.<sup>4</sup> However, a solvent like acetonitrile (polar, aprotic, possessing some nucleophilic and basic properties) may be used for certain purposes if freshly treated with activated neutral alumina.<sup>5</sup>

Under such experimental conditions, anisole<sup>4</sup> leads to the formation of 4,4'-dimethoxy biphenyl (solvent CH<sub>2</sub>Cl<sub>2</sub>/CF<sub>3</sub>COOH, 2/1 v/v). However, as it is the case for most of the coupling products of aromatic ethers, the so-formed dimer is more easily oxidized than the starting product. Therefore, at the electrolysis potential of anisole, dimer radical cation and even dication can be obtained :



The isolated yield of the dimer strongly depends on the stabilization of the oxidation products. This model reaction was widely generalized by Parker's group in order to synthesize a large range of polyether dimers.<sup>6</sup>

However, as shown by Parker and Bechgaard<sup>7</sup> in 1972, veratrole (orthodimethoxybenzene) leads in a one-pot reaction to the trimer (hexamethoxytriphenylene (T) with R = Me).

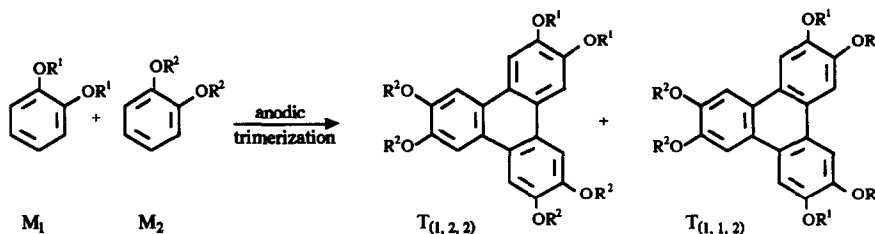


Similarly, electrolysis conditions allow the direct formation of trimer cation radical. When using exhaustive classical electrolysis cells, anodic method cannot be considered as the best one for the selective formation of trimers since a final reduction of  $T^{\cdot+}$  is needed. However, alternative chemical oxidative methods (for example : use of chloranil<sup>8</sup> or ferric chloride<sup>9</sup>) do exist. They are at the basis of the synthesis of liquid crystals derived from triphenylenes when R groups possess a long chain.<sup>10</sup>

Rather recently, it was demonstrated that the trimerization reaction was useful in the polymerization propagation of dibenzo-crown ethers<sup>11</sup> (electroformation of polytriphenylenes possessing complexing cavities for inorganic cations). In the meanwhile, trimers (T) bearing three complexing centers were formed electrochemically directly from monobenzo-crown ethers<sup>12,14</sup> when using redox cells equipped with porous electrodes. In certain cases insoluble but conductive deposits form at the anode: it was demonstrated that this solid phase corresponds to a mixed valency salt<sup>13</sup> of general formula  $T_2^+$ ,  $A^-$ ;  $A^-$  is the electrolyte anion.

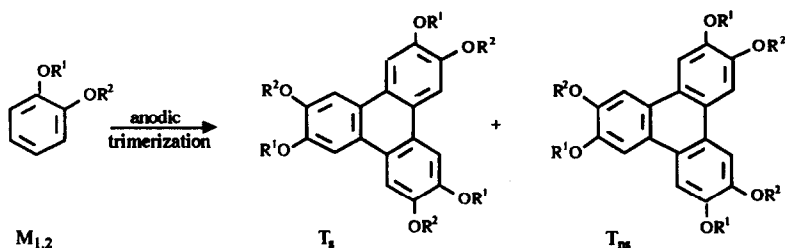
The aim of the present paper is to go deeply into the knowledge of anodic trimerization reaction already described :

(i) by means of the study of mixed trimerization processes using the coupled oxidation of two different monomers. In such a case, four products are expected :



together with  $T(1, 1, 1)$  and  $T(2, 2, 2)$

(ii) by trimerization of unsymmetrical dietheral monomers. Therefore, the oxidation should lead to a mixture of two triphenylenes :



Here, isomers  $T_s$  and  $T_{ns}$  correspond to sequenced and non sequenced trimers respectively.

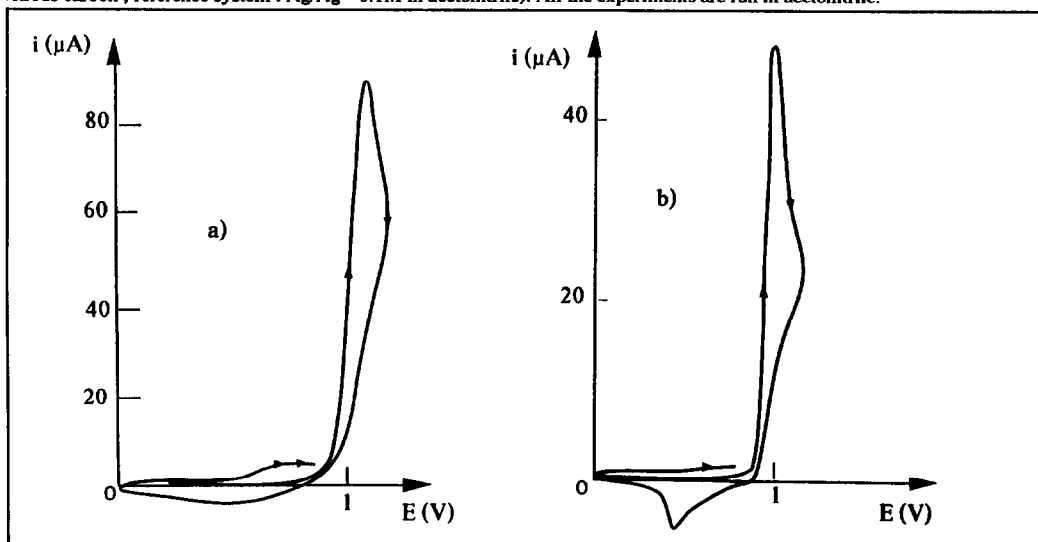
The present work reports preliminary results in this field of the anodic formation of those new substituted triphenylenes.

## EXPERIMENTAL

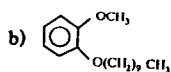
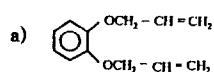
### I- Electrochemical equipment.

#### Cyclic voltammtries.

These are performed with a PAR Model 173 potentiostat equipped with a PAR Model 179 digital coulometer, a PAR Model 175 Universal Programmer and a Sefram X-Y recorder. Analytical studies presented in Figure 1 are performed in a microcell (total volume : 6 ml) using a polished platinum electrode ( $1\text{mm}^2$ ) sealed in soft glass as the working electrode (counter electrode : vitreous carbon ; reference system :  $\text{Ag}/\text{Ag}^+ 0.1\text{M}$  in acetonitrile). All the experiments are run in acetonitrile.



**Figure 1 :** cyclic voltammograms in acetonitrile containing :  $10^{-2}\text{M}$   $\text{NBu}_4\text{BF}_4$ , under inert atmosphere of argon (sweep rate :  $0.1\text{V}\cdot\text{s}^{-1}$  ; working electrode : polished platinum : area  $1\text{mm}^2$ ), substrate concentration  $0.2\text{M}$ .



**Macroelectrolysis.**

Preparative scale macroelectrolyses are carried out in an U-shaped two compartment cell (total volume : 150 ml). Anodic deposits are obtained on rectangular platinum foils (10 cm<sup>2</sup>). The counter electrode generally consists in a rod of vitrous carbon and the reference system remains Ag/Ag<sup>+</sup> 0.1 M in acetonitrile.

**Solvents and supporting electrolytes.**

They are carefully purified prior to use, according to previously described procedures.<sup>13</sup>

**II - Preparative electrolyses.**

Preparative electrolyses all carried out on 0.4 g of monomer lead either to insoluble trimers (as a conductive deposit on the anode) or soluble in the anolyte. In the first case, paramagnetic anodic deposits have to be detached from the platinum electrode. After being filtered and rinsed by technical acetonitrile, those mixed valency salts are reduced by triethylamine according to the following procedure : 0.2 g of trimers in mixture are treated by 20 ml of acetonitrile or pentane containing 2 ml of triethylamine. The duration of contact is two hours. The mixture of trimers is easily obtained after evaporation. In the absence of solid deposit onto the anode (second case), the anolyte solution (70 ml) is taken from at the end of the electrolysis ( $I_{end} < 10\% I_{start}$ ) and then directly treated by 7 ml of triethylamine. It has to be underlined that the use of a trialkylamine allows very conveniently to reduce doped conductive polymers and mixed valency salts according to a very recent procedure<sup>15</sup>. After a time of contact of two hours at room temperature, trimer mixture is extracted with ether.

Triphenylenes are separated by column chromatography using silica (Merk 60G) as a solid phase. The choice of the eluent depends on the nature of trimers to separate (see entries 7 to 15). After separation, trimers are characterized by all normal available methods.

**1) Synthesis of new symmetrical trimers.**

Entry N°	Monomer	E <sub>p</sub> (V)	E <sub>applied</sub> (V)	Trimer isolated yield (%)
1		1.09	1.05	25
2		1.18	1.15	19
3		1.05	1.00	25
4		1.05	1.03	10
5		1.05	1.00	35
6		1.13	1.10	-

**Table 1 :** Formation of T(1, 1, 1) trimers. E<sub>p</sub> corresponds to the peak potential in cyclic voltammetry under identical experimental conditions.

**Entry n°1 :** m/z = 564 - 60 MHz NMR (CDCl<sub>3</sub>) ppm (TMS) : 7.8 (s, 6H), 5.9 - 6.5 (m, 6H), 5.2 - 5.8 (m, 12H), 4.6 - 4.9 (m, 12H), m.p. (chloroform-pentane) : 165°C.

**Entry n°2 :** m/z = 402 - 300 MHz NMR (CDCl<sub>3</sub>) ppm (TMS) : 7.77 (s, 6H), 4.35 (s, 12H), m.p. (methylene chloride/pentane) : >300°C.

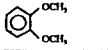

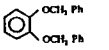

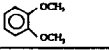

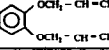

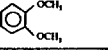

**Entry n°3 :** m/z = 1165 - 60 MHz NMR (CDCl<sub>3</sub>) ppm (TMS) : 7.8 (s, 6H), 4.1 - 4.3 (t, 12H), 0.6 - 2.2 (m, 114H), m.p. : (nitromethane) 54°C.

**Entry n° 4** :  $m/z = 864$  - 60 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.1 - 7.7 (m, 30H), 5.2 (s, 12H), m.p. (methylene chloride-pentane) : 186°C.

**Entry n° 5** :  $m/z = 408$  - 60 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.65 (s, 6H), 4.10 (s, 18H), m.p. (chloroform-pentane) : 297°C.

**Entry n° 6** : a totally insoluble solid compound is obtained which could not be purified or identified, m.p. : >300°C.

## 2) Mixed electrolyses.

Entry N°	M <sub>1</sub>	M <sub>2</sub>	E <sub>applied</sub> (V)	Trimer total yield (%)	T(1, 1, 1) yield (%)	T(2, 2, 2) yield (%)	T(1, 1, 2) yield (%)	T(1, 2, 2) yield (%)
7			1.10	30	57	8	14	21
8			1.02	22	26	23	25	26
9			1.01	30	36	3	26	35
10			1.02	not calculated	50	-	25	25
11			1.00	not calculated	50	-	30	20

**Table 2** : mixed electrolyses of monomers M<sub>1</sub> and M<sub>2</sub> always in equal molar concentration ( $8.3 \cdot 10^{-3} \text{ M} \leq \text{C} \leq 15 \cdot 10^{-3} \text{ M}$ ). Trimer yields are always relative isolated yields.

**Entry n° 7** : chromatographic separation : eluent : methylene chloride/ether (95/5, v/v).

T(1, 1, 2),  $m/z = 406$  - 60 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.90 (s, 2H), 7.70 - 7.75 (d, 4H), 4.45 (s, 4H), 4.10 (s, 12H), m.p. (methylene chloride-pentane) : 203°C.

T(1, 2, 2),  $m/z = 404$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.85 - 7.86 (d, 4H), 7.73 (s, 2H), 4.40 (s, 8H), 4.07 (s, 6H), m.p. (methylene chloride-pentane) : 229°C.

**Entry n° 8** : chromatographic separation : eluent : methylene chloride/pentane (9/1, v/v).

T(1, 1, 2),  $m/z = 764$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.30 - 7.77 (m, 26H), 4.40 (s, 8H), 4.07 (s, 6H), 5.31 - 5.55 (m, 2H), 5.31 - 5.55 (m, 12H), 4.72 - 4.75 (m, 4H), m.p. (methylene chloride-pentane) : 152°C.

T(1, 2, 2),  $m/z = 664$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.33 - 7.80 (m, 16H), 6.15 - 6.22 (m, 4H), 5.34 - 5.56 (m, 12H), 4.74 - 4.82 (m, 8H), m.p. (methylene chloride-pentane) : 141°C.

**Entry n° 9** : chromatographic separation : eluent : methylene chloride/ether (97/3, v/v).

T(1, 1, 2),  $m/z = 460$  - 60 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.60 (s, 2H), 7.45 (s, 4H), 5.95 - 6.60 (m, 2H), 5.20 - 5.85 (m, 4H), 4.70 - 4.90 (m, 4H), 4.10 (s, 12H), m.p. (methylene chloride-pentane) : 148°C.

T(1, 2, 2),  $m/z = 512$  - 60 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.75 - 7.85 (d, 4H), 7.68 (s, 2H), 5.95 - 6.60 (m, 4H), 5.25 - 5.80 (m, 8H), 4.73 - 4.90 (m, 8H), 4.10 (s, 6H), m.p. (methylene chloride-pentane) : 172°C.

**Entry n° 10** : chromatographic separation : eluent : methylene chloride/pentane (9/1, v/v).

T(1, 1, 2),  $m/z = 496$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.78 - 7.81 (t, 6H), 6.16 - 6.25 (m, 4H), 6.10 (s, 2H), 5.51 - 5.58 (m, 4H), 5.34 - 5.39 (m, 4H), 4.81 - 4.85 (m, 8H), m.p. (methylene chloride-pentane) : 171°C.

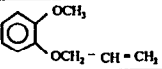
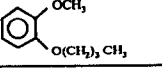
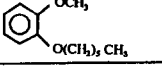
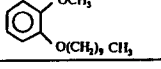
T(1, 2, 2),  $m/z = 428$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.76 - 7.78 (d, 6H), 6.14 - 6.27 (m, 2H), 6.10 (s, 4H), 5.50 - 5.58 (m, 2H), 5.34 - 5.39 (m, 2H), 4.81 - 4.84 (m, 4H), m.p. (methylene chloride-pentane) : 190°C.

**Entry n° 11** : chromatographic separation : eluent : methylene chloride/ethyl acetate (95/5, v/v).

T(1, 1, 2),  $m/z = 392$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.81 - 7.88 (m, 6H), 6.11 (s, 2H), 4.10 (s, 12H), m.p. (methylene chloride) : >300°C.

T(1, 2, 2),  $m/z = 376$  - 300 MHz NMR ( $\text{CDCl}_3$ ) ppm (TMS) : 7.77 - 7.85 (t, 6H), 6.11 (s, 4H), 4.10 (s, 6H), m.p. (methylene chloride) : >300°C.

3) Electrolyses of unsymmetrical orthodiethers.

Entry N°	M <sub>1,2</sub>	E <sub>p</sub> (V)	E <sub>applied</sub> (V)	Trimer total yield (%)
12		1.05	1.03	23
13		1.04	0.99	32
14		1.01	0.95	26
15		1.01	0.96	20

**Table 3 :** electrolyses of unsymmetrical orthodiethers M<sub>1,2</sub> (1.57 10<sup>-2</sup> M ≤ C ≤ 2.44 10<sup>2</sup> M).

The structure of the two isomers T<sub>NS</sub> and T<sub>S</sub> was assigned thanks to <sup>1</sup>H NMR. For that, T<sub>S</sub> exhibits only two different types of aromatic hydrogen (two singlets of equal intensity) while T<sub>NS</sub> possesses four different types of hydrogen (four singlets grouped in a multiplet with the relative intensities : 2:1:1:2). Such assignment may be checked if necessary by 300 MHz NMR : the three R<sub>1</sub> and R<sub>2</sub> signals respectively are equivalent (T<sub>S</sub>) or non equivalent (T<sub>NS</sub>).

**Entry n° 12 :** Trimers in mixture ; T<sub>NS</sub> (75 %) + T<sub>S</sub> (25 %). m/z = 486 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 7.84 - 7.97 (q, 6H), 5.99 - 6.12 (m, 3H), 5.40 - 5.48 (q, 6H), 4.56 - 4.60 (m, 6H), 3.68 - 3.70 (q, 9H). The ratio of the two isomers is estimated from NMR data.

**Entry n° 13 :** chromatographic separation : eluent : ether/petroleum ether (1/1, v/v).

T<sub>NS</sub>, m/z = 534 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.09 (s, 2H), 8.06 (s, 1H), 8.00 (s, 1H), 7.96 (s, 2H), 4.04 - 4.08 (t, 6H), 3.70 - 3.71 (d, 9H), 1.73 - 1.82 (m, 6H), 1.47 - 1.57 (m, 6H), 0.85 - 0.93 (m, 9H), m.p. (methylene chloride-pentane) : 106°C.

T<sub>S</sub>, m/z = 534 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.10 (s, 3H), 8.03 (s, 3H), 4.04 - 4.08 (t, 6H), 3.69 (s, 9H), 1.75 - 1.84 (m, 6H), 1.49 - 1.59 (m, 6H), 0.88 - 0.93 (t, 9H), m.p. (methylene chloride-pentane) : 148°C.

**Entry n° 14 :** chromatographic separation : eluent : methylene chloride/pentane (9/1, v/v).

T<sub>NS</sub>, m/z = 618 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.14 (s, 2H), 8.09 (s, 1H), 8.02 (s, 1H), 7.97 (s, 2H), 4.07 - 4.11 (m, 6H), 3.72 (s, 9H), 1.80 - 1.85 (q, 6H), 0.86 - 1.51 (m, 27H), m.p. (methylene chloride-pentane) : 100°C.

T<sub>S</sub>, m/z = 618 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.11 (s, 3H), 8.03 (s, 3H), 4.06 - 4.11 (t, 6H), 3.71 (s, 9H), 1.81 - 1.86 (m, 6H), 0.86 - 1.50 (m, 27 H), m.p. (methylene chloride-pentane) : 82°C.

**Entry n° 15 :** chromatographic separation : eluent : methylene chloride/ethyl acetate (95/5, v/v).

T<sub>NS</sub>, m/z = 786 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.16 (s, 2H), 8.11 (s, 1H), 8.03 (s, 1H), 7.98 (s, 2H), 4.09 - 4.15 (m, 6H), 3.73 (d, 9H), 0.90 - 1.88 (m, 57H), m.p. : 56°C.

T<sub>S</sub>, m/z = 786 - 300 MHz NMR (C<sub>6</sub>D<sub>6</sub>) ppm (TMS) : 8.13 (s, 3H), 8.04 (s, 3H), 4.09 - 4.14 (t, 6H), 3.72 (s, 9H), 0.89 - 1.88 (m, 57H), m.p. : 70°C.

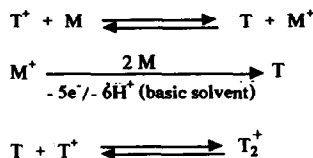
**DISCUSSION**

Several aromatic orthodiethers possessing alkoxy substituents OR<sup>1</sup> and OR<sup>2</sup> with R<sup>1</sup> and R<sup>2</sup> equal to methyl, allyl, n-hexyl, n-decyl, benzyl, etc... may be converted by anodic synthesis into more or less complex hexasubstituted triphenylenes. In electrolyses of mixtures all the possible different isomers were isolated and identified as shown by results gathered in Tables 1, 2 and 3.

First of all, overall yields when using a classical cell are rather limited (of the order of 30 %). However, it is worth underlining that attempts to form such mixed trimers by the chemical method (principally

by use of  $\text{FeCl}_3$ ) have failed so far. Redox cells with a porous anode - whose interest was already mentioned by our group <sup>14</sup> - while giving slightly better yields were not utilized for this preliminary study. As a matter of fact, anodic precipitations may rapidly plug up electrode pores. On the other hand, a fine balance of electrolyses was necessary (e.g. case where 4 trimers were expected to be formed) and a complete work up of both deposits and anolyte solution has to be carried out.

Stabilization of oxidized forms of triphenylenes can be understood in a speculative way implying the charge transfer complex formation (soluble or not) between  $\text{T}^+$  and T (leading to  $\text{T}_2^+$  which requires somewhere an electron transfer from the monomer).



Experimentally, for electricity consumptions larger than one electron per mole, one observes the disappearance of the monomer from the anolyte without a net increase of the trimer yield. At the same time, small amounts of quinones can be detected. Concerning mixed oxidations of  $\text{M}_1$  and  $\text{M}_2$  (gathered in Table 2), it obviously appears that the applied potential plays a major role in the product distribution. As example given by the entry n°7,  $\text{M}_1$  is oxidized less positively than  $\text{M}_2$  and this should favor strongly the preferential formation of  $\text{T}_{(1, 1, 1)}$ . On the contrary, when  $\text{M}_1$  and  $\text{M}_2$  exhibit nearer  $E_p$  values (understood roughly as a similar anodic reactivity) the trimer distribution appears (at least for entry n°8) to be more homogeneous. We are far, however, from a purely statistical distribution which should strongly favor the two mixed trimers. But oppositely, trimerization of dissymmetrical orthodiesters  $\text{M}_{1,2}$ , apparently not depending on the applied voltage leads to isomer mixtures in good agreement with what is expected from a statistical rate ( $\text{Tns}/\text{Tis}$  ratio always of the order of 3 : 1).

Additional work is in progress both for synthesizing a broader palette of such complex trimers, in order to use them as liquid crystals and carry out their specific electrocrystallization. Moreover scaling up the electrochemical formation of those given mixed trimers is obviously an exciting goal.

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