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ELECTROSYNTHESIS OF 2,2',6,6'-TETRAARYL 4,4'-BIPYRANNYLIDENES WITH EIGHT FLEXIBLE CHAINS.

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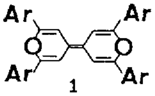
SUMMARY
2,2',6,6'-tetraaryl 4,4'-bipyrannylidenes with eight flexible chains are synthesized by electrochemical reduction of the corresponding 2,6-diarylpyrylium salts.

2,2',6,6'-tetraaryl 4,4'-bipyrannylidene 1 can be synthesized by chemical reduction of 2,6 pyrylium salts 2 with zinc powder.

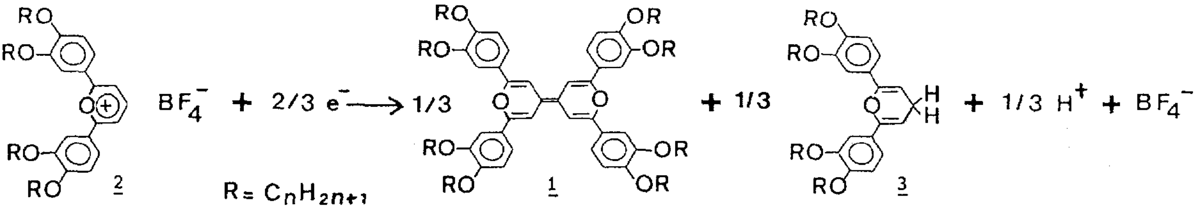


1

2

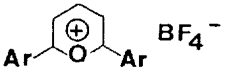
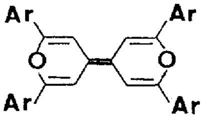
This process reported[1] for $Ar=C_6H_5$, $X=ClO_4^-$ has been generalized to many other pyrylium salts 2 (Ar=p-alkylphenyl, monoalkoxyphenyls, p-carboalkoxyphenyls, etc)[2,3]. Conjugated heterocycles 1, powerfull π-donors lead to conducting paramagnetic species[3]. When each aryl group possesses one long flexible chain, the 2,2',6,6'-tetraaryl 4,4'-bipyrannylidenes 1 give, with crystalline acceptors like TCNQ, liquid-crystalline conductors[3,4].

In order to enhance mesomorphic and π-donor behavior of 1, we wanted to obtain heterocycles 1 in which each aryl group was substituted by two alkoxy chains. In this case, chemical reduction by zinc failed. We tried to obtain such compounds by electrosynthesis. Electrochemical reduction of pyrylium salts has already been studied[5,6]. 2,2',6,6'-tetraaryl 4,4'-bipyrannylidene 1 have been electrosynthesized starting from 2 (Ar=Ph)[5] or from the corresponding thiopyrones ($Ar=p\text{-}RO\text{-}C_6H_4$)[7]. We have been able to synthesize 2,2',6,6'-tetraaryl 4,4'-bipyrannylidenes 1 bearing eight alkoxy chains by electrochemical reduction of pyrylium fluoroborates 2 (Ar = 3,4-dialkoxyphenyl) according to the reaction[8]:



A typical procedure is as follows: the electrosynthesis was conducted in a divided cell (cathode: gold gauze, anode: platinum gauze). The catholyte was a solution of the 2,6-diarylpyrylium salts 2[10], 0.5 mmol in 30 ml of CH_2Cl_2 containing nBu_4NBF_4 0.1 M as the supporting electrolyte. The electrolysis conducted at a controlled potential (Table 1) afforded the 2,2',6,6'-tetraaryl 4,4'-bipyrannylidene 1 which precipitated in the cell. The electrolysis afforded also soluble 2,6-diarylpyrane 3[11]. The solid products 1 isolated after filtration of the catholyte were washed with acetonitrile or dichloromethane and were recrystallized from chloroform. Table 1 lists experimental conditions of the electrosyntheses.

Table 1: electrosynthesis of bipyrannylidenes 1.

	 Ar 2	F/mol[8]	E^1 (V) (a)	RECOVERED 2 %	 1 %(b)
	C_6H_5 (c)	0.70	-0.38	12	61(d)
2a	3,4-$(CH_3O)_2C_6H_3$	0.88	-0.40	0	45
2b	3,4-$(C_4H_9O)_2C_6H_3$	0.70	-0.46	17	68
2c	3,4-$(C_{10}H_{21}O)_2C_6H_3$	0.95	-0.49	0	63

(a): E^1: reduction peak potential of the starting pyrylium salt 2 and potential of the electrolysis. The potentials (at a steady gold disk electrode ϕ=1mm) are relative to a SCE electrode. Scan rate of 0.2 Vs^{-1}. nBu_4NBF_4 0.1M. (b): isolated, percentages are based on the theoretical yield of 1/3 of the converted pyrylium salt. (c): electrolysis conducted in CH_3CN. (d): identified by comparison to an authentic sample[2].

The new bipyrannylidenes 1 were characterized by their oxidation potentials (Table 2) and their UV (Table 3), ^1H NMR (Table 4), IR and Mass spectra[12].

Table 2: oxidation potentials of 1

	Ar	E^2 (V)	E^3 (V)	ΔE (V)
	C_6H_5	0.25	0.72	0.47
1a	3,4-$(CH_3O)_2C_6H_3$	0.04	0.56	0.52
1b	3,4-$(C_4H_9O)_2C_6H_3$	0.12	0.38	0.36
1c	3,4-$(C_{10}H_{21}O)_2C_6H_3$	0.14	0.48	0.34

E^2, E^3 : oxidation peak potentials of the bipyrannylidenes 1 in cyclic voltammetry in the same conditions as mentionned in Table 1. The two peaks are reversible as already observed for less substituted compounds[3].

Table 3: UV vis. spectra of 1

	concentration mol.l^{-1}	λ_{max}(nm) at t_o	λ_{max}(nm) at t	t (mn)
1b	$3x10^{-6}$	616	532	1290
1b	$1.3x10^{-6}$	616	532	650
1c	$8x10^{-5}$	632	532	1410

Solvent: $CHCl_3$. t represents the time when the absorption of the species at 616 nm (1b) or at 632 nm (1c) is only 20% of the initial absorption (t_o). The absorption at 532 nm is at that time maximum.

A microscopic examination of compounds 1b and 1c shows indication of mesomorphic properties in contrast to tetra substituted analogs[3]. X-Ray studies are in progress in order to confirm these properties.

When characterizing the bipyrannylidenes 1, we concluded that they were self-associated in aggregats. First we found that the UV spectra of compound 1b and 1c were different as a function of the concentration and time (Table 3).

Concentrated solutions of compounds 1b and 1c ($C > 10^{-4}$ M) are blue and stable with time. More diluted solutions are first blue and become red with time. Results in Table 3 show that the more diluted the solutions are the faster they turn red. It seems that solutions are blue when aggegats are present and red when not present, that means at low concentration. Similar conclusions have been mentionned for bipyrannylidenes with four long alkyl chains[13]. The examination of ^{1}H NMR spectra (Table 4) leads to the same conclusion.

Table 4: ^{1}H NMR spectra of bipyrannylidenes 1.

	C mol.l^{-1}	t°C	$OCH_2C_{n-1}\underline{H}_{2n-1}$ (ppm)				$OC\underline{H}_2$ (ppm)		aromatic and vinylic $\underline{H}$ (ppm)			
1c	10^{-2}	20	0.90 24 H	1.31 96 H	1.57 16 H	1.88 16 H	4.10 16 H		–	–	–	–
1c	2.7×10^{-3}	20	0.90 24 H	1.30 96 H	1.54 16 H	1.91 16 H	4.22 8 H	4.30 8 H	7.26 4 H	8.03 4 H	8.70 4 H	9.58 4 H
1b	2×10^{-3}	20	1.01 24 H	1.55 16 H	1.82 16 H		4.15 16 H		–	–	–	–
1b	2×10^{-3}	50	1.03 24 H	1.58 16 H	1.89 16 H		4.23 8 H	4.30 8 H	7.20 4 H $23^{(a)}$	8.00 4 H $30^{(a)}$	8.56 4 H $45^{(a)}$	9.47 4 H $60^{(a)}$

Solvent: $CDCl_3$. ^{1}H NMR spectra have been run at 400 MHz for compound 1b and at 250 MHz for compound 1c. (a): $\Delta\nu_{1/2}$=width of the signal at half-height in Hz.

A ^{1}H NMR spectrum of a concentrated solution of compound 1c (Table 4) shows only the signals characteristic of the aliphatic protons of the side chains $OC_{10}\underline{H}_{21}$ without detection of the aromatic and vinylic protons. The same sample after dilution exhibits the aromatic and vinylic protons as broad signals.

A ^{1}H NMR spectrum of compound 1b (Table 4) run at room temperature shows only the signals characteristic of the aliphatic protons $OC_4\underline{H}_9$. The aromatic and vinylic protons have been detected only at higher temperature as broad signals. We ascribe this phenomenon to variations in the proton relaxation with the degree of association. If the molecules are self-associated, the protons belonging to the core of the association are unable to relax[14]. However higher temperature or lower concentration leads to desaggregation and easier relaxation of the aromatic and vinylic protons.

Electrochemical reduction of pyrylium salts 2 thus appears to be a suitable method to synthesize bipyrannylidenes 1 bearing eight flexible chains. 2,2',6,6'-tetra(p-hydroxyphenyl) 4,4'-bipyrannylidene[15] has been also synthesized by electrochemical reduction of the corresponding pyrylium salt. In this case its synthesis by zinc reduction of the pyrylium salt failed.

Work is in progress to better characterize these bipyrannylidenes bearing eight flexible chains, to determine the size of the aggregates and the properties of the mesomorphic structures. A fully detailed study of the mechanism and determination of the electron stoichiometry of this electrosynthesis of bipyrannylidenes based upon voltammetric data will be soon published[9].

ACKNOWLEDGEMENTS

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8. The electron stoichiometry is based upon cyclic voltammetric experiments[9]. In Table 1, the charge consumed exceeds 0.66 F/mol owing to partial electrolysis of the solvent/supporting electrolyte system.
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11. The 2,6-diphenylpyrane has been isolated and compared to an authentic sample prepared according to: H.M. WHITBOCK, N.A. CARLSON, Tetrahedron, 20,2101(1964). Attempt to isolate the 2,6 diarylpyrane 3 in the case of compounds 1b and 1c led to their hydrolysis product: Ar-CO-$(CH_2)_3$-CO-Ar
    Ar=3,4-dibutyloxyphenyl:^1H NMR (250 MHz in $CDCl_3$): 1ppm t 12H, 1.5ppm m 8H, 1.83ppm m 8H, 2.18ppm m 2H, 3.08ppm t 4H, 4.08ppm t 8H, 6.92ppm d 2H J=8.5Hz, 7.58ppm d 2H J=2Hz, 7.62ppm dd 2H J=8.5Hz J=2Hz.
    Ar=3,4-didecyloxyphenyl:^1H NMR (250 MHz in $CDCl_3$): 0.89ppm t 12H, 1.3ppm m 48H, 1.48ppm m 8H, 1.85ppm m 8H, 2.18ppm m 2H, 3.07ppm t 4H, 4.08ppm t 8H, 6.92ppm d 2H J=8.5Hz, 7.6ppm d 2H J=2Hz, 7.64ppm dd 2H J=8.5Hz J=2Hz.
12. Compound 1a: dark red solid. IR(KBr): 1630cm^{-1}. UV(in chloroform):λ_{max} = 516 nm. Mass: MH^+= 705.
    Compound 1b: dark blue solid. IR(KBr): 1635cm^{-1}.Mass MH^+= 1041, $M/2H^+$= 521.
    Compound 1c: dark blue solid. IR(KBr): 1635cm^{-1}.
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15. Dark red solid. IR(KBr): 1630cm^{-1}. UV(in methanol): 473, 360, 314, 270 nm. Mass: MH^+= 529, $M/2H^+$= 265.

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